ELSEVIER

Biochimica et Biophysica Acta 1412 (1999) 1–28

BIOCHIMICA ET BIOPHYSICA ACTA

BBA

www.elsevier.com/locate/bba

Review

Chlorophyll *a* fluorescence induction[1]

Dušan Lazár *

Department of Experimental Physics, Faculty of Science, Palacký University, tř. Svobody 26, 771 46 Olomouc, Czech Republic

Received 24 March 1998; received in revised form 23 February 1999; accepted 11 March 1999

Keywords: Chlorophyll *a* fluorescence induction; Electron transport; Excitation energy transfer; Model

Contents

1. Introduction 2
   1.1. Chlorophyll fluorescence 2
   1.2. Fluorescence induction 2
   1.3. F_0, F_M and F_V/F_M parameters 3

2. Fluorescence induction measured under low light illumination 4
   2.1. Fluorescence rise measured with DCMU - PS II antenna heterogeneity 4
   2.2. Fluorescence rise measured without DCMU - PS II reducing side heterogeneity 6
   2.3. Decrease in fluorescence after its maximal value 8

3. Fluorescence induction measured under high light illumination 9

4. Pump and probe technique 11

5. Changes in fluorescence induction caused by different effects 12
   5.1. Effect of elevated temperature 12
   5.2. Other effects (oxygen, bicarbonate, phosphorylation) 13

6. Mathematical description of fluorescence induction 13
   6.1. Models of Photosystem II function and photosynthetic unit(s) 13
   6.2. Fluorescence intensity dependence on state of Photosystem II 16
   6.3. Results of the mathematical modelling of fluorescence induction 20

Abbreviations: CA, complementary area; DCMU, 3-(3′,4′-dichlorophenyl)-1,1-dimethylurea; F_0, minimal fluorescence intensity; F_M, maximal fluorescence intensity; F_V, variable fluorescence ($F_V = F_M - F_0$); F_V/F_M, maximal quantum yield of Photosystem II photochemistry; FI, fluorescence induction; HCO_3^-, bicarbonate; NH_2OH, hydroxylamine; OEC, oxygen evolving complex; P680, the primary electron donor in Photosystem II; PAP, pump and probe; Pheo, the primary electron acceptor in Photosystem II (pheophytin); PQ, plastoquinone; PS I, Photosystem I; PS II, Photosystem II; PS IIα, Photosystem II alpha; PS IIβ, Photosystem II beta; PSU, photosynthetic unit; Q_A, the primary quinone electron acceptor in Photosystem II; Q_B, the secondary quinone electron acceptor in Photosystem II; RC II, reaction centre of Photosystem II; RRP, reversible radical pair; Y_Z, the secondary electron donor in Photosystem II (tyrosine 161)

* Fax: +42 (68) 522-5737; E-mail: lazard@risc.upol.cz

[1] Dedicated to Docent Jan Nauš on the occasion of his 50th birthday.

PII: S0005-2728(99)00047-X

Acknowledgements 22

References 22

1. Introduction

Chlorophyll *a* fluorescence induction (FI) is now a widespread method used in photosynthesis research. This is because FI is non-invasive and highly sensitive, fast and easily measured, it requires relatively inexpensive equipment, and it contains important information about the photosynthetic apparatus. Even though FI has been measured for more than 60 years, a full theory of FI does not exist yet and in many cases photosynthesisers do not interpret their FI data precisely. The 'wrong' situation with FI led Holzwarth [1] to ask the question: 'Is it time to throw away your apparatus for chlorophyll fluorescence induction?'. In my opinion, the situation with FI is not 'so bad' since several reasonable theories for FI exist although they are valid when several assumptions and restrictions are made; this will remain true until a new and a better theory is available. However, a lot of research on chlorophyll *a* FI is still necessary so that we could paraphrase Holzwarth's statement to the form 'There is no reason to throw away our apparatus for chlorophyll fluorescence induction.'. This review is focused on the latest explanations for the origin of particular steps involved in the course of FI. Also an explanation of terms used in connection with FI is covered in this review. When it is necessary, the readers are referred to other review articles.

1.1. Chlorophyll fluorescence

The quantum yield of chlorophyll *a* fluorescence in a solution (where excitation energy transfer and photochemistry do not occur) is about 20–35% [2] and this fluorescence has a lifetime of about 6–20 ns [3–5]. On the other hand, the quantum yield of chlorophyll *a* fluorescence from the photosynthetic apparatus is only about 2–8% (from open to closed reaction centres of Photosystem II, RC II) [2,6] with an average lifetime of about 300 ps (for open RC II) [7–10] and about 1.6 ns (for closed RC II[2]) [7,8]. At room temperature fluorescence is mainly emitted from Photosystem II (PS II) [19,20]. The contribution of Photosystem I (PS I) to the fluorescence signal at room temperature is about 20% [6,21,22]. But at emission wavelengths greater than 700 nm the contribution can be up to 50% in C_4 plants [325]. Nevertheless, in a first approximation, which is well accepted by photosynthesisers, FI is understood to originate from PS II.

1.2. Fluorescence induction

The discovery of the fluorescence induction phenomenon is attributed to Kautsky and Hirsch [23] who wrote in 1931 the first scientific paper on this topic. Thus, FI is often referred to as the Kautsky effect. The authors saw with their eyes a time course of fluorescence intensity and correlated it qualitatively with the time course of CO_2 assimilation published earlier by Otto Warburg. During 1934–1960, Kautsky and his students published 13 papers on FI (see [24,25]). For a discussion of FI in the early stage of its research see refs. [26–30].

FI represents a plot of the measured fluorescence intensity as a function of time of continuous illumination. The term FI is understood as fluorescence rise in this review and a decrease in fluorescence over a long time scale (also called slow FI in the literature) is discussed only briefly. FI can be measured by different fluorometers (see [31] for a recent review on commercial fluorometers), but the shape of the FI measured with control plant material mainly

[2] RC II was firstly isolated by Namba and Satoh [11] and it is composed of D1-D2-cytochrome b_{559} complex plus psb-I gene product. RC II includes 6 chlorophylls *a*, 2 pheophytins and 2 β-carotenes [12–17] and is isolated without Q_A and Q_B (the primary and secondary quinone electron acceptor in PS II, respectively). Although RC II has also been isolated with Q_A and Q_B [18], this procedure did not find a practical usage. However, when speaking about RC II in the following text, Q_A and Q_B are presumed to be present. Open RC IIs are then understood as those RC IIs which can undergo a charge separation and stabilisation whereas closed RC IIs cannot.

differs depending on used light illumination for the measurements. Thus, FIs measured under low and high light illuminations are discussed separately in this review. Fluorescence saturation curve measured using the pump and probe technique is also discussed.

The graphs of courses of FIs measured with different experimental set-ups together with an explanation of the nomenclature are presented in appropriate sections below. For further information on the nomenclature of FI and chlorophyll *a* fluorescence in general see [20,25,32–41].

1.3. F_0, F_M and F_V/F_M parameters

As every FI curve goes from minimal fluorescence intensity F_0 to maximal fluorescence intensity F_M, their meaning is explained here together with the meaning of the F_V/F_M parameter. The value of minimal fluorescence intensity is usually denoted by the letter F with the subscript 0 but also with the subscript o or simply as Fo. The letter o stands for origin [42,43] and capital O is usually used in the graphic presentation of minimal fluorescence intensity in the FI curve. On the other hand, the value of maximal fluorescence intensity is usually denoted by the letter F with the subscript m or M or max. When it is supposed that at the position of the P step in FI, where the letter P stands for peak [42,43], fluorescence intensity denoted as F_P reaches its maximum, then $F_M = F_P$ (the equality holds only for high light illumination and the appropriate time of illumination, see Section 2). Then, the equality can be extended to $F_V/F_M = F_V/F_P$, where F_V ($F_V = F_{M(P)} - F_0$) is the variable fluorescence. However, very good correlation between the parameters F_V/F_M and F_V/F_P was also found for low light illumination [44].

Among others, Butler [45,46] postulated that fluorescence originates from the chlorophylls of the light harvesting antenna. Minimal fluorescence F_0 is then an emission from these excited chlorophylls in PS II antenna in competition to excitation energy transfer to RC II. It takes place before excitons reach RC IIs; it is an emission when RC IIs are open [47,48]. On the other hand, it has been suggested that the exciton can visit photochemical molecule P680 (the primary electron donor of PS II) many times before photochemistry occurs [326–329]. Thus, the minimal fluorescence F_0 might also reflect the excitation loss during this process. However, both previous processes, i.e., the energy transfer to P680 and the unsuccessful trapping of the excitons by P680 for photochemistry, but also trapping of the excitons for photochemistry and other energy loss processes are described by the transfer equilibrium of excitons in PS II antenna and RC II as derived by Laible et al. [49]. Thus, it has been suggested that the non-zero value of F_0 is a consequence of the transfer equilibrium [50]. It is also possible that not all the chlorophylls in the PS II antenna are functionally connected to RC II [33,46], F_0 can also include contributions from these chlorophylls [51,52]. This part of F_0 has been called F_N (N means non-active) and forms the main part of F_0 in the early stage of the greening of plants [53]. It is also possible that a part of F_0 may also come from initially closed RC IIs [54]. Since a direct measurement of the quantum yield of charge separation in functional RC II complexes leads to a value of about 1 [55], a lower value of the F_V/F_M parameter (0.832) as an expression of the maximal quantum yield of PS II photochemistry (see below) may be caused by an increase of F_0 due to the initially blocked (damaged) RC IIs. This interpretation is consistent with the known turnover of the D1 protein of PS II [56] and with a proposed PS II repair cycle [57]. It was experimentally found [58–61] and theoretically derived [19] that F_0 comes mainly from PS II, which agrees with the results of Trissl et al. [6] who found that the contribution of PS I emission to F_0 is about 20%. An increase of F_0 under stress conditions, when F_M remained constant, is probably caused by a decrease in the overall rate constant for the utilisation of excitons for photochemistry [62]. This is in agreement with the results that a slight increase in F_0 is caused by a partially reversible decrease in the quantum yield of PS II photochemistry, whereas a higher increase in F_0 probably originates from an irreversible disconnection of the small light harvesting complex of PS II [10]. It was derived that the value of F_0 (also F_M) does not depend on the model used for a photosynthetic unit [61,63,64] (see Section 6).

It is generally accepted that the maximal fluorescence intensity F_M expresses the state of PS II when all Q_A (the primary quinone electron acceptor in PS II) molecules are reduced [65,66]. It was found that

under a short high light single turnover flash the fluorescence intensity does not reach its maximal value [67] and that the maximum is obtained only after a high light illumination lasting at least 200 ms [68]. Thus it was recommended not to use short flashes for the determination of F_M because this underestimates the F_V/F_M ratio [68].

Kitajama and Butler [61] showed that the maximal quantum yield of PS II photochemistry, Φ_P, can be expressed as $\Phi_P = (F_M - F_0)/F_M = F_V/F_M$. The measurement of the F_V/F_M parameter with 44 different plant species showed that the mean value of this parameter is 0.832 [69]. On the other hand, the immediate quantum yield of PS II photochemistry (at any time t under actinic illumination) $\Phi_P(t)$ can be accurately approximated as $\Phi_P(t) = (F_M'(t) - F(t))/F_M'(t)$ [70], where $F_M'(t)$ and $F(t)$ denote the maximal fluorescence obtained with a saturating flash at time t and fluorescence at time t obtained under actinic light illumination, respectively. But when the reversible radical pair model (RRP, see Fig. 6), proposed by van Grondelle [71], has been applied to energetically connected PS IIs, a correction C for the previous expression has been found [63,64]: $\Phi_P^{RRP}(t) = C\Phi_P(t)$, where $\Phi_P^{RRP}(t)$ denotes the immediate quantum yield of PS II photochemistry determined according to [63,64]. The constant C was found to depend only on the rate parameters of RC II and the omission of C in $\Phi_P(t)$ underestimates it by about 14% [63,64].

Even if the F_0, F_M, and F_V/F_M parameters (and also other fluorescence parameters determined from FI) are almost always presented by the mean and standard deviation (or standard error) in the literature (see, e.g., [69]), it need not be correct. On the basis of statistical testing of the values of these parameters it has been found that this kind of data presentation masks the real data distribution of the parameters and the use of median, quartiles and maximal and minimal values is recommended [72].

2. Fluorescence induction measured under low light illumination

The fluorescence rise measured during low light illumination and with control plant material is shown in Fig. 1, curve a. The fluorescence rise was firstly

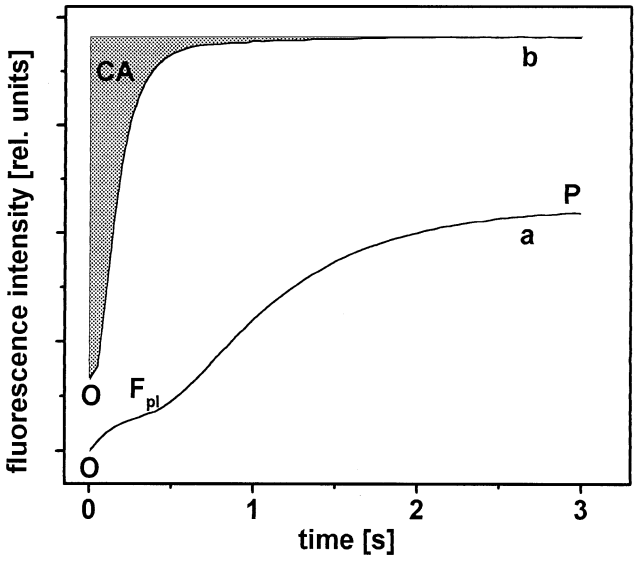

Fig. 1. Fluorescence rise measured with dark adapted (20 min) pea leaves under low light illumination (40 μmol m^{-2} s^{-1} of red light with maximum at about 650 nm). Curve a, control leaf; curve b, DCMU-treated leaf (200 μM, 2 h). The O and P steps and the plateau F_{pl} are marked. CA means the complementary area.

denoted as O–P (means origin and peak) according to [42,43] and an intermediate plateau between the O and P steps as F_{pl} according to [66]. The plateau is also marked as I (inflection) and sometimes there is a dip D after the I step [47,73]. However, very often the fluorescence rise is measured in the presence of the PS II herbicide 3-(3′,4′-dichlorophenyl)-1,1-dimethylurea (DCMU) (Fig. 1, curve b). This is because DCMU blocks electron transport from Q_A to Q_B (the secondary quinone electron acceptor in PS II) by displacing Q_B from the Q_B pocket of D1 protein of PS II [74–77] and thus the situation in the plants is simpler in comparison with DCMU-untreated plant material where Q_B and the plastoquinone pool are involved in the electron transport chain. For this reason, the fluorescence rise measured with and without DCMU are discussed separately, starting with the former.

2.1. Fluorescence rise measured with DCMU - PS II antenna heterogeneity

It was found that the fluorescence rise measured with DCMU-treated plant material cannot be de-

scribed by a single exponential increase [78]. The shape of the FI measured with DCMU is complicated and usually sigmoidal. This sigmoidal fluorescence rise (see Fig. 1, curve b) is usually explained on the basis of antenna heterogeneity, i.e., different types of PS IIs. These PS IIs differ mainly in their light harvesting antenna. However, this type of PS II heterogeneity is very tightly connected with the excitation energy transfer between photosynthetic units which is discussed in Section 6.

Bennoun and Li [79] found a correlation between the increase in fluorescence in the presence of DCMU and the rate of hydroxylamine (NH_2OH, donor of electrons to PS II) oxidation. The number of molecules of oxidised NH_2OH accumulating with increasing time of illumination can be obtained by integrating the NH_2OH-oxidation curve. This is equivalent, due to the existing correlation, to a computation of the area over the fluorescence rise (the complementary area and referred to as CA) measured with DCMU. The CA is an area between the curve of FI and line determining the level of the maximal fluorescence intensity F_M (see Fig. 1, curve b). As in the case of DCMU-treatment the electrons are transported only to Q_A, the time course of the CA expresses the time dependence of the number of reduced Q_A. This was later proved to be true when a correlation between the time course of the CA and the time dependence of the number of reduced Q_A (monitored by 320 nm absorption changes which reflects the Q_A reduction) was found [80]. These results were theoretically derived already a long time before [81,82] and have been recently confirmed by numerical and analytical results based on the RRP model [6,63,64]. A proportionality constant between the CA and the number of reduced Q_A was also derived [63,64].

The evaluation of the time course of the CA as outlined before has been used by Melis and Homann [83,84] for a description of one type of PS II heterogeneity, the PS II antenna heterogeneity. These authors found that there is a biphasic behaviour of the time course of the CA increase. This behaviour was attributed to two different types of PS IIs denoted as PS IIα and PS IIβ. Besides the different relative amount of PS IIβ in plant material (20–35% [63,64,85–87]) these PS IIs have a smaller rate constant k_β, which characterises the rate of PS IIβ photochemistry, than k_α of PS IIα. As the quantum yield of charge separation is the same in PS IIα and PS IIβ [88,89], the smaller rate constant k_β in comparison with k_α of PS IIα expresses the smaller PS II antenna of PS IIβ [80]. PS IIβ differs from PS IIα, among other things, in the fact that the former has an exponential fluorescence rise (in the presence of DCMU) in comparison with PS IIα which has a sigmoidal one. It is generally accepted that the exponential increase in fluorescence intensity reflects energetic separation of PS IIβ [80,90,91]. The energetic separation means that when the exciton comes to a closed RC II of PS IIβ, there is no possibility to transfer the exciton to any other PS IIβ. However, it was shown [92–94] that an exponential increase in fluorescence intensity can also be obtained assuming a statistical model of PSU (see Section 6) which supposes energetic communication without any restriction. This is in agreement with the later result of Lavergne and Leci [95] that when there is a small amount of PS IIs (up to 40%) responsible for the exponential fluorescence rise (PS IIβ), the exponential increase need not indicate that there is no energetic communication between the PS IIs. The energetic communication means that the exciton after visiting the closed RC II can be transferred to any other RC II, namely, without any restriction (i.e., statistical model of PSU) or with a restriction (i.e., model of connected PSUs, see Section 6). On the other hand, the sigmoidal increase in fluorescence intensity is believed to reflect restricted energetic communication between PS IIα (see Section 6). However, simulations based on the RRP model have led to the sigmoidal increase in fluorescence intensity even with an assumption of energetic communication without any restriction between PS IIs [6] (see Section 6 for more details).

Although the procedure of PS IIα and PS IIβ determination suffers from the uncertainty of F_M determination [96,97], it has been used for the determination even of three (α, β, γ) [97] or four (α, β, Γ, δ) [98] different types of PS II. An improved mathematical procedure used for the determination of this type of PS II heterogeneity which does not suffer from the erroneous F_M determination was proposed by Hsu et al. [99] where the authors distinguished between three types of PS II firstly called α, α-s, and β [99] and lately renamed to α, β, and γ [100], respectively.

There are also other procedures that deals with the determination of this type of PS II heterogeneity. One procedure uses a method of moments ensuring an evaluation of the correct number of exponential rise components in the increase in fluorescence intensity measured in the presence of DCMU [101]. Using this method, three types of PS II (α, β, γ) were determined. On the other hand, by using equations describing the RRP model within the connected PS IIs (see paragraph above), two different types of PS II (α, β) were distinguished [63,64] from the FI measured with DCMU present. This procedure is probably the best one for determination of this type of PS II heterogeneity because it is based on the latest results (the RRP model) and the procedure directly fits the increase in fluorescence intensity instead of the evaluation of the CA and thus avoids possible mistakes [63], rising from erroneous determination of F_M.

Note that the same notation for the PS IIs by different authors need not mean the same type of PS II. For further details on PS II antenna heterogeneity, see other review articles [102–106].

It is necessary to point out that at the time when the PS II antenna heterogeneity was not known, the sigmoidal increase in fluorescence intensity measured with DCMU present was explained on the basis of the reduction of more then one PS II electron acceptor [107,108]. Possible excitation energy transfer from closed RC IIs (Q_A reduced) to other RC IIs and rate constants of RC IIs reactions were thought to be reasons for the sigmoidal increase in fluorescence intensity (see Section 6). As mentioned above, the assumption of the energetic connectivity is now used for PS IIα. The sigmoidal course of fluorescence rise was also explained on the basis of the domain theory of PS II where a limited number of PS II exists in one domain and the excitation energy transfer is not restricted within the domain. The best fit to the experimental FI measured with DCMU was found for 3–5 PS IIs in one domain [64,92] or under the assumption that there are two PS IIα in one domain and one PS IIβ, with an antenna size of 41% of PS IIα, in another domain [109]. An aggregation of 4–5 PS IIα into one domain was also found from a different initial (determined for zero time) and final (determined at the end of the contribution of PS IIα to fluorescence rise measured with DCMU) values of k_α [90]. Also an accumulation of triplet states [59,110–113] and annihilation processes [92,114–116] (see also Section 6) can significantly change the fluorescence signal.

The evaluation of the time course of CA was also used to suggest other PS II electron acceptor(s) in addition to Q_A [81,82,117]. From the smaller value of F_M measured with DCMU in comparison with F_M measured without DCMU (both measured under high light illumination), it has been suggested that the oxidised plastoquinone (PQ) pool can act as a non-photochemical quencher of fluorescence [118–120].

2.2. Fluorescence rise measured without DCMU - PS II reducing side heterogeneity

The exponential increase in fluorescence intensity to the plateau F_{pl} in the FI measured without DCMU (see Fig. 1, curve a) observed by Melis [85] and the same value of the rate constant of this increase and that of k_β determined from the FI measured with DCMU led him to a suggestion that F_{pl} reflects PS IIβ. In spinach leaves, this PS IIβ cannot reduce Q_B and the PQ pool – the Q_B-nonreducing RC II. Thus, a new kind of PS II heterogeneity – reducing side heterogeneity was born. Many researchers in photosynthesis also call the Q_B-nonreducing RC II inactive RC II. This is based on the original observation of Graan and Ort [121] that there is a different number of RC II determined on the basis of the use of different artificial PS II electron acceptors. These authors explained this observation assuming the existence of RC IIs inactive in Q_B (PQ pool) reduction.

It is necessary to point out that F_{pl} reflects the amount of Q_B-nonreducing RC IIs only when low illumination (about 10–50 μmol $m^{-2}\,s^{-1}$) and eventually artificial electron acceptors are used. This treatment leads to a state in which in the Q_B-reducing RC IIs the rate of Q_A^- oxidation exceeds the rate of Q_A reduction and that is why the Q_B-reducing RC IIs do not contribute to F_{pl}. As the electrons cannot be transferred from Q_A^- to Q_B in the Q_B-nonreducing RC IIs, the electrons accumulate on Q_A in these RC IIs and thus the relative height of F_{pl} in comparison to F_M reflects the relative amount of Q_B-nonreducing RC IIs [85,122]. In this way it was found that there

are between 7% and 35% of the Q_B-nonreducing RC IIs [85,86,95,123,124].

The hypothesis that F_{pl} reflects the amount of Q_B-nonreducing RC II was first suggested by Melis [85] even if the author (and also many other researchers) referred to the work of Forbush and Kok [66]. But the latter authors have only suggested that under low light illumination, the Q_A^- (from the Q_B-reducing RC II) cannot accumulate at F_{pl} since electrons are quickly transported out to the subsequent PS II acceptor(s). These authors explained the increase in fluorescence intensity to F_{pl} by the activation process of Q_A proposed earlier by Joliot [125] (the activation process can be described by the reactions $Q_i \rightarrow Q^-$ and $Q^- + A \rightarrow Q + A^-$, where Q_i is the 'inactive' Q_A, A is an electron acceptor after Q_A, and Q is the 'active' Q_A, and it was further supposed that Q_i is formed from Q in dark). Nevertheless, it is clear that the activation process used for an explanation of the results in [66,125] was a reduction of Q_A in the Q_B-nonreducing RC II as is well accepted now.

A similar situation exists with the terms Q_B-reducing and Q_B-nonreducing RC IIs. Many researchers refer to Lavergne [126,127] as the discoverer of this type of PS II heterogeneity. But Lavergne had found that after the addition of DCMU only about 50% of the fluorescence intensity originates from the backward electron transport from Q_B^- to Q_A. The PS II electron acceptors where the backward electron transport occurs Lavergne had called the B type (B stands for today's Q_B) and other PS II electron acceptors the non-B type. The non-B type acceptors are thus the acceptors which can transport electrons from Q_A further (anywhere) even if DCMU is present. Thus, the non-B type acceptors are different from the Q_B-nonreducing RC IIs which cannot transfer electrons to Q_B. Hence, there is an equivalence only between the terms Q_B-nonreducing RC II and inactive RC II and thus, reference for Q_B-nonreducing RC II to Lavergne's work [126,127] is incorrect. Even Lavergne himself has pointed out [106] that except for a nomenclature ambiguity, there is no relation between his non-B type acceptors and today's Q_B-nonreducing RC IIs.

The amount of Q_B-nonreducing RC IIs as determined from the relative height of F_{pl}, seems to be incorrect, even when low light illumination is used. Hsu [128,129] has found by a simulation that the fluorescence rise to F_{pl} can be also affected by the equilibrium between the forward and backward electron transport between Q_A and Q_B in the Q_B-reducing RC II. Thus, 5–10% of Q_A from the Q_B-reducing RC IIs can be reduced in the time the plateau is reached and contribute by 30–65% to the fluorescence intensity F_{pl}, depending on the used illumination [128]. As the improbable values of some rate constants were used in the simulation leading to the 65% contribution to the fluorescence intensity F_{pl}, the contribution of the Q_B-reducing RC IIs by 30% to the fluorescence intensity F_{pl} is more realistic value. On the other hand, excluding the possibility of the Q_B-reducing RC IIs to contribute to the fluorescence rise from F_0 to F_{pl}, this rise also depends on the state of OEC and its contribution can be 35–45% of F_{pl} [95,129]. Finally, even after subtracting the contribution of OEC to the F_{pl}, the resulting relative value of fluorescence intensity does not reflect the relative amount of Q_B-nonreducing RC II but $1/(1-p)$ times less (p is a connectivity parameter; see Section 6) as was suggested on the basis of theoretical calculations based on possible excitation energy transfer between PS IIs [95].

It is clear from the results above that the fluorescence rise to the plateau is a photochemical phase since it is related to reduction of Q_A^- (mainly of Q_B-nonreducing RC II but also to some extent of Q_B-reducing RC II). As the fluorescence rise to the I_1 step (or to the J step) of FI measured under high light illumination has also been identified as the photochemical phase (see Section 3), the fluorescence rise to the plateau measured under low light illumination and fluorescence rise to the I_1 step (or to the J step) measured under high light illumination should be identical in their origin.

Sometimes when the FI is measured without DCMU there is no plateau before fluorescence reaches the maximum P but the fluorescence intensity goes through an intermediate maximum I and a consequent dip D before reaching P. The existence of the dip D was attributed to the activation processes (as mentioned above) [130] and to the dynamic equilibrium between PS II and PS I [47,130]. A time delay from zero time after which the fluorescence intensity increases from the plateau (or I–D transient) to the P step was used as a measure of the rate of PQ reduction in Q_B-reducing RC IIs [62,131]. An increase in

the time delay means a decrease in the reducing activity of PS II.

On the basis of mathematical simulations and fitting of the experimental FI measured without DCMU it was found that an accumulation mainly of $Q_AQ_B^-$ and $Q_AQ_B^{2-}$ forms occurs at the position of the plateau [132,133]. However, because these forms do not include Q_A^-, they cannot cause the increase in fluorescence (see Section 6). Nevertheless, there is a gradual accumulation of $Q_A^-Q_B^{2-}$ in the time between the plateau and P [132] which is the main reason why fluorescence increases. The relative amount of accumulated forms in particular steps is, however, intensity dependent and thus also the height of the particular steps in the fluorescence rise is intensity dependent (see [34]). Thus, under low light illumination even in the P step not all Q_A and Q_B are reduced and the P step then does not indicate the maximal fluorescence intensity. This is demonstrated in Fig. 1: low light illumination is not sufficient to close all the RC IIs which results in the P step being smaller (Fig. 1, curve a) than the maximal fluorescence intensity measured with DCMU (Fig. 1, curve b) where the herbicide helps the low light illumination to close all the RC IIs and thus to reach the real F_M value. From the fitting of the theoretical model to the experimental fluorescence rise measured without DCMU it was also found that a gradual increase in the reduced PQ pool occurs during the rise with a maximum at the P step. However, even in the P step not all the PQ pool is reduced [132].

For review articles on PS II reducing side heterogeneity, see other references [102–106,134–137].

2.3. Decrease in fluorescence after its maximal value

The time courses of the decrease in fluorescence after its maximal value has been reached are shown in Fig. 2. The decrease in fluorescence was firstly denoted as $P \rightarrow S \rightarrow M \rightarrow T$ according to [138] (Fig. 2, curve a); however, additional local maxima can be present and then the decrease is denoted as $P \rightarrow S_1 \rightarrow M_1 \rightarrow S_2 \rightarrow M_2 \rightarrow T$ according to [139] (Fig. 2, curve b). Description of the fluorescence decrease is complicated because too many events happen simultaneously on this time scale and that is why it is difficult to find a precise explanation of the particular steps during the decrease.

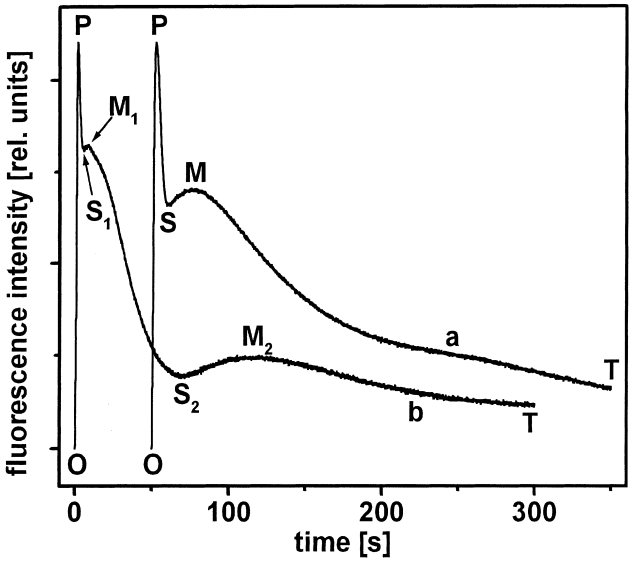

Fig. 2. Decrease in fluorescence after its maximum measured with control dark adapted (20 min) pea leaves under low light illumination (40 μmol $m^{-2} s^{-1}$ of red light with maximum at about 650 nm). The O, P, S, M and T steps (curve a, shifted by 50 s to the right) and the O, P, S_1, M_1, S_2, M_2 and T steps (curve b) are marked.

As the time range of the whole decrease in fluorescence is large, it is probable that the changes in the absorption cross-section of PS II occur during the decrease which are caused by a long-lasting illumination [25]. The decrease in fluorescence has also been related to changes in the rate of carbon metabolism [140–142] and oxygen evolution [141]. The oxygen in the air can probably accept electrons which, in addition to the draining of electrons from the PS II acceptor side by PS I, can cause the decrease in fluorescence [47,130,143]. The role of oxygen evolution in the course of the decrease in fluorescence should also be considered as implied from a comparison with the simulation of time course of oxygen evolution based on a model of the function of OEC [144]. The decrease in fluorescence also depends on the pH of the suspension used [145], the proton gradient across the thylakoid membrane [146–148], Mg^{2+} concentration [149–152], and the involvement of photoreduction of the primary electron acceptor in PS II, pheophytin (Pheo), was also suggested [153].

Any decrease in fluorescence is nowadays understood as fluorescence quenching. Thus, the decrease in fluorescence after the P step can be discussed in the light of quenching analysis involving photochem-

ical and non-photochemical quenching. But, as many review articles have been written on this topic (see [20,34,37,41,50,154,155]) and because it is not the main aim of this review to describe this technique and all its results in detail, only a brief overview follows.

Based on the work of Bradbury and Baker [156], Schreiber et al. [157] designed a pulse fluorescence method which makes it possible to determine whether photochemical and/or non-photochemical quenching, characterised by q_P and q_N quenching coefficients, respectively, cause a decrease in the fluorescence signal. It has been found that photochemical quenching, in contrast to non-photochemical quenching, decreases with increasing light illumination [158–160]. The overall non-photochemical quenching may be separated into three components [158–160]: high-energy state (related to the acidity of thylakoid lumen [146]), photoinhibitory (related to non-radiative energy dissipation due to excessive illumination [161]) and state-transition (related to the redistribution of excitation energy from PS II to PS I [162]) non-photochemical quenching, characterised by q_E, q_I and q_T quenching coefficients, respectively. State-transition non-photochemical quenching is predominant under low light illumination whereas high-energy state and photoinhibitory non-photochemical quenching are involved mainly under high light illumination [158–160]. Also different dark relaxation kinetics has been found for each non-photochemical quenching mechanism with a half time of about 1 min, 4–10 min and hours for high-energy state, state-transition and photoinhibitory non-photochemical quenching, respectively [159,160].

From the intensity dependence of particular types of fluorescence quenching one may suggest that the decrease in fluorescence after the P step as shown in Fig. 2, i.e., under low light illumination (40 μmol $m^{-2} s^{-1}$) is mainly caused by photochemical and state-transition non-photochemical quenching. On the other hand, the decrease in fluorescence after the P step measured under high light illumination is mainly caused by high-energy state and photoinhibitory non-photochemical quenching. When speaking only about photochemical and (overall) non-photochemical quenching, both should be responsible for the decrease in fluorescence after the P step measured under low light illumination, (overall) non-photochemical quenching being dominant in high light illumination as measured in [156,157].

The decrease in fluorescence intensity from the P step to the terminal T step has been suggested to be a measure of the potential photosynthetic capacity of photosynthetic apparatus which is evaluated as $R_{fd} = (F_P/F_T) - 1$, where F_P and F_T denote fluorescence intensities at the P and T steps, respectively [163].

3. Fluorescence induction measured under high light illumination

The measurement of fluorescence induction under extremely high light illumination is presented in Fig. 3A. The extremely high light illumination allows to distinguish two steps between minimal and maximal fluorescence intensity denoted as I_1 and I_2 [67,68,164] and sometimes also a dip D_1 after the I_1 step. The O–I_1 transient was suggested [67,68] to be equivalent to the photochemical phase of FI found under extremely high light illumination [165] which reflects the reduction of Q_A. On the other hand, the I_1–D_1–I_2–M transient was called the thermal phase because it depends on the temperature of measurement [68]. It was suggested that the D_1–I_2 transient reflects the activity of OEC [164].

The measurement of FI with the Plant Efficiency Analyser (PEA, Hansatech, Norfolk, UK) enabling the measurements of the fluorescence intensity 10 μs after the onset of actinic light was first introduced by Strasser and Govindjee [166,167]. A typical time course of FI as measured by the PEA fluorometer and with control plant material is shown in Fig. 3B, curve a. There are two steps again between minimal and maximal fluorescence intensity, denoted as J and I, which are clearly distinguished when a logarithmic time-axis is used. The J, I and P steps appear at about 2 ms, 20 ms and 200 ms, respectively; however, the time of appearance of each particular step is intensity dependent [39]. On the basis of the same intensity dependence found for the J and I steps [39] and for the I_1 and I_2 steps [68] it has been established that there is an equivalence of the J step with the I_1 step and the I step with the I_2 step [39]. The equivalence is expected because also the O–I_1–I_2–M curve presented on a logarithmic time-axis (inset of

Fig. 3A) and the O–J–I–P curve (Fig. 3B, curve a) are practically the same. Thus, except for graphic presentation where the O–J–I–P curve is always presented on a logarithmic time-axis whereas the O–I_1–I_2–M curve not, there is no difference between these two 'types' of FI. However, we recommend that the cumbersome terms I_1 and I_2 be dropped in favour of J and I.

Strasser and Govindjee [167] have suggested that the J step reflects an accumulation of $Q_A^-Q_B$ form which was shown to be correct by experimental results and theoretical simulations [39,54,168–173]. An accumulation of Q_A^- in the J step was also demonstrated by an increase in fluorescence in this step after the addition of DCMU [39,174–176]. As the accumulation of Q_A^- occurs in the position of the J step, this step is called the photochemical phase [39] in accordance with the photochemical phase of FI measured in [165] and the I_1 step [68]. This photochemical phase is, however, shifted to a shorter time in comparison with the fluorescence rise to the plateau which represents the photochemical phase of FI measured under low light illumination (see Section 2). The shift to the shorter time of the photochemical phase in the case of FI measured under high light illumination is caused by faster rate of Q_A reduction due to high light illumination which agrees with the disappearance of the J step when FI is measured by PEA fluorometer under low light illumination [39,174,177,178]. Thus, the new step in FI measured under high light illumination is the I step (or the I_2 step) and not the J step (or the I_1 step) as might have been incorrectly concluded from the measurements of FI with the higher time resolution by PEA fluorometer. It has also been found that the relative height of the J step does not depend on the size of the PS II antenna [179].

The I step has been suggested to reflect an accumulation of $Q_A^-Q_B^-$ form, whereas the P step an accumulation of $Q_A^-Q_B^{2-}$ form [167]. The results of mathematical simulations show that at the position of the I step accumulation of $Q_A^-Q_B^{2-}$ and $Q_A^-Q_BH_2$ forms occurs (Q_BH_2 means the protonated form of Q_B^{2-}). The same holds for the P step but there is a further increase in the $Q_A^-Q_BH_2$ form [54,168–173]. As in the case of FI measured under low light illumination, not all PQ pool is reduced in the position of the P step [170,172,173]. Reduction of two types of PQ pool, fast and slow, may be reflected in the I and P steps [39,101,179].

The FI was also measured using a He–Ne laser, beam of which was modulated by an acoustooptic modulator (Bragg cell) which allowed the measurement of the same FI as with PEA fluorometer, i.e., from 10 μs upwards [174,175,177,178]. The instrument used measured the FI simultaneously at 685

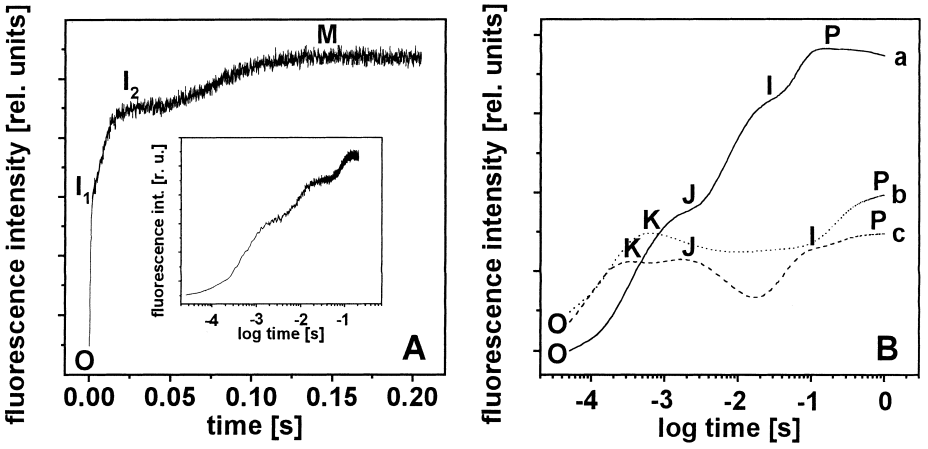

Fig. 3. (A) Fluorescence rise measured with control dark adapted (20 min) tobacco leaf under extreme high light illumination (9000 μmol $m^{-2}\,s^{-1}$ of white light). The O, I_1, I_2 and P steps are marked. The same curve is presented on logarithmic time-axis in the inset. (B) Fluorescence rise measured with dark adapted (20 min) pea (curves a and b) and potato (curve c) leaves under high light illumination (3400 μmol $m^{-2}\,s^{-1}$ of red light with maximum at about 650 nm). Curve a, control leaf; curve b, leaf incubated at 47°C for 5 min; curve c, leaf incubated at 44°C for 13 min. The O, K, J, I and P steps are marked, being clearly distinguished only on logarithmic time-axis.

and 730 nm and thus one could evaluate the parameter $R(t) = F730(t)/F685(t)$, where $F730(t)$ and $F685(t)$ are the time courses of fluorescence intensity measured for emission at 730 nm and 685 nm, respectively. The time course of $R(t)$ is characterised by an initial value of R_0, two local minima R_b and R_p (at times of 20–80 ms and 1–1.5 s, respectively), and a stationary value R_s [178]. As there are no changes in the absorbance of the leaves during the decrease from R_0 to R_b, the decrease reflects changes in the fluorescence spectrum [178]. On the other hand, the time course of $R(t)$ from 100 ms upwards reflects changes in leaf absorbance [178,180,181] and changes in excitation energy transfer between PS II and PS I [182]. From the $R(t)$ it is possible to evaluate the adaptation index A_p as $A_p = 1-(R_p/R_s)$, which provides information about the possibility of the photosynthetic apparatus to adapt to changes in light conditions [182].

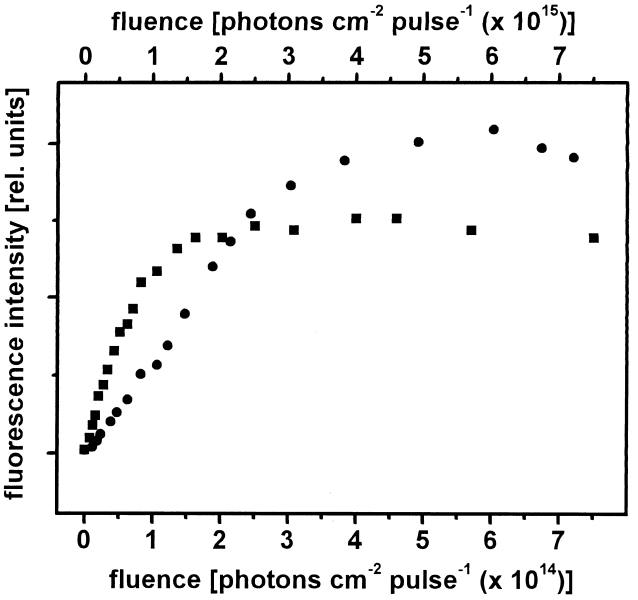

Fig. 4. Fluorescence rise measured with spinach chloroplasts by PAP technique. Squares (bottom x-axis), t_1 of pump pulse 0.7 μs (dye laser, 650 nm) probed after 100 μs by pulse of microseconds (xenon lamp). Circles (top x-axis), t_1 of square pump pulse 13 ms (He–Ne laser, 632.8 nm) probed after 5 ms by pulse of 2 μs (xenon lamp), 10 μM DCMU.

4. Pump and probe technique

When FI is measured using the pump and probe (PAP) technique, the sample is illuminated by an actinic excitation pulse (pump pulse) of length t_1, and after a different time-lag, the fluorescence of the sample is detected using a weak measuring pulse (probe pulse) of different length. FI measured using the PAP technique is then presented as a plot of fluorescence intensity as a function of the amount of photons which hit the sample area per pump pulse (see Fig. 4). France et al. [183] have found that the course of PAP FI does not depend on the presence of DCMU, the length of the time-lag between pump and probe pulses, and the length of a probe pulse but it is only determined by t_1: if $t_1 < 300$ ps, the PAP FI is clearly exponential in shape [183], if 0.7 μs $< t_1 <$ 2 μs (Fig. 4, squares) then the PAP FI is almost exponential in shape [94,183–192] and finally if $t_1 > 50$ μs (Fig. 4, circles) then the PAP FI is sigmoidal in shape [94,183]. If t_1 is of order of milliseconds then the course of PAP FI (measured with DCMU) is the same as the course of FI (with DCMU) measured under continuous illumination [183]. A threshold time t_1 which leads to the change from the exponential to the sigmoidal shape of PAP FI is in a range of 2–50 μs [94,183]. There is an increase of F_M/F_0 parameter with increasing t_1: $F_M/F_0 < 3$ when $t_1 < 2$ μs and $F_M/F_0 > 3$ when $t_1 > 50$ μs [94,183].

The change of the shape of PAP FI was explained on the basis of the double hit model [94,183] which involves changes of RC II through four different states. In this model a dark time-lag t_0 is important which converts one state of RC II to another one and thus enables the effective utilisation of the 'double hit' for photochemistry. If $t_1 < t_0$ then PAP FI is exponential in shape otherwise it is sigmoidal. From the experimental results and theoretical simulations it was suggested [94] that the length of t_0 which determines the shape of PAP FI is in a range of 0.4–10 μs. On the basis of the double hit model, the well-known equation for the dependence of fluorescence intensity on the amount of closed RC II (Eq. 4 in Section 6) was determined [94] independent of the length of t_1. The model mentioned above is based on a simpler double hit model suggested in [108] which can also explain both the exponential and sigmoidal course of FI. However, the results of [94,183] were not confirmed in [193] where the authors found that the

course of PAP FI is always sigmoidal in shape no matter how long t_1 is. The authors [193] have suggested that the dependence of PAP FI on t_1 found in [94,183] were caused by the oxidation of Q_A^- through Q_B and by a recombination of Q_A^- with the S_2 state of OEC (when DCMU is present), and thus the authors [193] also threw doubt on the double hit model proposed in [94].

The pulse length results of PAP FI measurements have been reconsidered in relation to singlet–triplet annihilation processes [115,116]. Valkunas et al. [116] have theoretically demonstrated (see Section 6) that the course of PAP FI strongly depends on the singlet-triplet annihilation processes and suggested that the annihilation processes are a more natural explanation for the observation in [94,183] than the double hit model proposed in [94]. The roles of singlet–singlet annihilation [114] and the accumulation of triplet states [111–113] on pulse length results of PAP FI measurements have also been studied.

5. Changes in fluorescence induction caused by different effects

5.1. Effect of elevated temperature

There are two main changes in the FI measured under low light illumination caused by elevated temperatures. The first one is a relative increase in the height of the plateau which indicates an increased amount of Q_B-nonreducing RC II. An increased amount of Q_B-nonreducing RC II is caused by the inhibition of electron transport form Q_A to Q_B which is reported to start from about 45°C [122,194–196]. On the other hand, up to 42°C there is no increase in the relative height of the plateau and thus no increase of Q_B-nonreducing RC IIs [62]. The second change in the course of FI caused by elevated temperatures is an increase in the time delay from zero time after which the fluorescence intensity increases from the plateau (or the I–D transient) to the P step [62]. The increase means that more time is needed to reduce the PQ pool. Such an increase starts from about 32°C [62].

There is an increase in the minimal fluorescence intensity F_0 with increasing temperature as can also be seen in FI measured under high light illumination [62,164]. In this type of FI measurement, the maximal fluorescence intensity F_M is already reached at the I_2 step for temperatures above 38°C [62,164].

After the heat stress of plant material at about 47°C (incubation for 5 min or by linear heating with rate 4°C min^{-1} to this temperature), a new step K at about 300 μs appears in the FI measured under high light illumination by PEA fluorometer (see Fig. 3B, curve b) [197–202]. The K step was measured even together with the J step in the FI curve (see Fig. 3B, curve c) which shows that the K step is not caused simply by the J step being at a shorter time [197–199]. Thus, it has been suggested that the K step is also present in the FI of control plants that did not have temperature stress, but for dynamic reasons the K step is not observed as a separate step [197–200]. It was suggested that the appearance of the K step is caused by the inhibition of OEC [197–200,333] which leads to an accumulation of the oxidised secondary electron donor of PS II - Y_Z (tyrosine 161 [232,233]) [200], as well as by the inhibition of the electron transport from Pheo to Q_A [197,198] leading to an accumulation of $P680^+Pheo^-$ [198]. Further, the appearance of the K step includes changes in the organization of the light harvesting antenna [199]. On the basis of the assumption that at the time of the K step appearance in FI an accumulation of Q_A^- occurs (i.e., the K step represents the photochemical phase of FI), it has been suggested that the decrease in fluorescence intensity after the K step reflects the oxidation of Q_A^- via subsequent electron acceptors of PS II [199,200]. But it has also been suggested that the decrease in fluorescence intensity after the K step is mainly caused by nonradiative charge recombination between $P680^+$ and Q_I^- [334]. All the results indicate that the K step appearance reflects an irreversible high temperature induced change of PS II [198,199,202].

It was found that the temperature of the K step appearance depends on the acclimation of the plant material to elevated temperatures [201,202] and that a correlation between changes in FI and the fluorescence temperature curve caused by high temperatures exists [202].

5.2. Other effects (oxygen, bicarbonate, phosphorylation)

When FI is measured under low light illumination with green algae and under a decreasing concentration of O_2, the following changes occur step by step: a loss of decrease in fluorescence from the P to the S steps, increase in F_0 and fluorescence intensity at the I step, and the appearance of the dip D after the I step [47,130,143,203,204]. Schreiber et al. [130] have suggested that the loss of decrease in fluorescence from the P to the S is caused by an inhibition of the reoxidation of the reduced PQ pool. These authors discussed the decrease in fluorescence intensity from the P step to the S step under aerobic condition in terms of: reoxidation of Q_A^- by PS I; acceptance of the electrons by oxygen; or by both effects. However, it is known that the pseudofirst order rate constant (incorporating the concentration of oxygen) for the oxidation of the reduced PQ pool is about 0.038 s^{-1} [205] which is too slow to be the only reason for the decrease in fluorescence intensity from P to S. But on the other hand, it implies from the measurements of the O_2 dependent electron transport [206,207] that the conditions for reduction of air oxygen are much better in lower plants as measured in [130] than in higher plants (see [208]). A strong decrease in O_2 leads to a drastic increase of F_0 after which the fluorescence intensity steadily decreases, indicating a complete malfunction of PS II [130]. On the other hand, a decreased amount of air oxygen mainly causes a reversible increase in the J step in FI measured by PEA fluorometer with pea leaves: the course of FI is similar to that measured with DCMU, indicating that electron transport after Q_A is inhibited [209]. The inhibition may be caused by a dark reduction of the PQ pool under anaerobic conditions [210–212]. The latest results suggest that the oxygen evolved by PS II can act as a quencher of fluorescence with a rate constant of about 400 s^{-1} [213].

It was found that a deficiency of bicarbonate (HCO_3^-) in PS II (caused by formate) leads to FI which is very similar to the FI measured with DCMU and that this effect is reversible [214]. Thus, it was suggested that HCO_3^- acts mainly on the acceptor side of PS II [214,215] even though it may also be necessary for the functioning of the donor side of PS II [216–218]. Bicarbonate binds to the non-heme iron between Q_A and Q_B [219,220] and thus HCO_3^- deficiency causes an inhibition of Q_B^{2-} protonation leading to a lack of Q_B^{2-} exchange with a PQ molecule from the pool [221–225].

The phosphorylation of PS II core does not change the O–I transient in the FI measured under low light illumination [226]. DCMU measurements of FI with phosphorylated samples show a decrease in F_V and an increased amount of PS IIβ [227]. However, the rate constants k_α and k_β of PS IIα and PS IIβ, respectively, do not change before and after phosphorylation in these measurements indicating that no change in the absorption cross-section of PS II occurred after phosphorylation [227]. On the other hand, measurement of FI, in the presence of DCMU, with a wheat mutant which is incapable of phosphorylation, shows only an exponential increase in fluorescence intensity which is also evident from the measurements of FI by the PAP technique [226]. As mentioned in Section 2, the exponential increase in fluorescence intensity reflects energetic separation of PS IIs. Similar conclusions were also obtained in [228] that the phosphorylation of membrane proteins decreases the connectivity between PS IIs.

6. Mathematical description of fluorescence induction

6.1. Models of Photosystem II function and photosynthetic unit(s)

Before a description of FI is formulated on the basis of which FI is simulated or a model can be fitted to the experimental data, a knowledge of the structure and function of PS II and its arrangement into photosynthetic unit(s) is required. Thus, a description of two (complementary) models of PS II function, which are well-accepted nowadays, and a description of the term photosynthetic unit(s) and the models for its/their arrangement is presented below.

The light reactions occurring in PS II may be divided into 'slow' and 'fast' ones depending on the value of the time constant of a particular reaction. Electron transport within PS II through Q_A and Q_B and the subsequent protonation of double reduced Q_B, its exchange with a PQ molecule from the PQ

pool and the oxidation of the reduced PQ pool by cytochrome b_6/f complex are considered as the 'slow' reactions which last from hundreds of microseconds to tens of milliseconds [25,229,230]. In addition to these events on the acceptor side of PS II, also reactions on the donor side of PS II (i.e., S-state transitions of OEC [231] and electron donation from Y_Z to $P680^+$) occur on a 'slow' time scale [25,229,230]. The electron transport between Q_A and Q_B is described by the well-known two-electron gate model (see Fig. 5) which treats the consequent electron transport from Q_A^- to Q_B and Q_A^- to Q_B^-, Q_B being a two-electron acceptor [234,235]. On the other hand, excitation energy transfer/equilibrium, charge separation, recombination, and stabilisation are considered as the 'fast' reactions, which last maximally hundreds of picoseconds [71,230,236]. P680, Pheo, Q_A and all the pigments from the PS II antenna participate in these reactions. It is accepted that such reactions are accurately described by the RRP model (also called the exciton–radical pair equilibrium model, Fig. 6) proposed in [71] (see also [22,237–239]). As knowledge of the rate constants of particular 'slow' and 'fast' reactions is essential for a full description of PS II function and thus for mathematical modelling of FI, they are listed in Table 1.

The photosynthetic apparatus is suggested to be arranged in photosynthetic unit(s) (PSU) [291,292] (see also [293] and a special issue of *Photosynthesis Research* honouring the discovery of the concept of PSU [330]). The PSU contains one or more P680s and its associated antenna pigments. The PSU models depend on the number of P680 in one PSU and the extent of excitation energy transfer within/between PSU. One possible arrangement of photosynthetic apparatus is in separated PSUs [117,294] where one PSU is formed by one P680 and its associated antenna pigments. The excitation energy transfer is only possible from the antenna pigments to the P680 within that specific PSU, but not to P680 in any other PSU. An opposite approach to the description of the photosynthetic apparatus is with the help of the statistical model [58–60,71,110,295,296]. In the statistical model, the complete photosynthetic apparatus is arranged in one PSU where many P680s are located in one reservoir of antenna pigments. Excitation energy can be transferred without any restriction from antenna pigments to any P680, as well as between P680s within the PSU. The separate PSU model and statistical model are also called the puddle model and the lake model, respectively, according to Robinson [331]. There are two other possible model

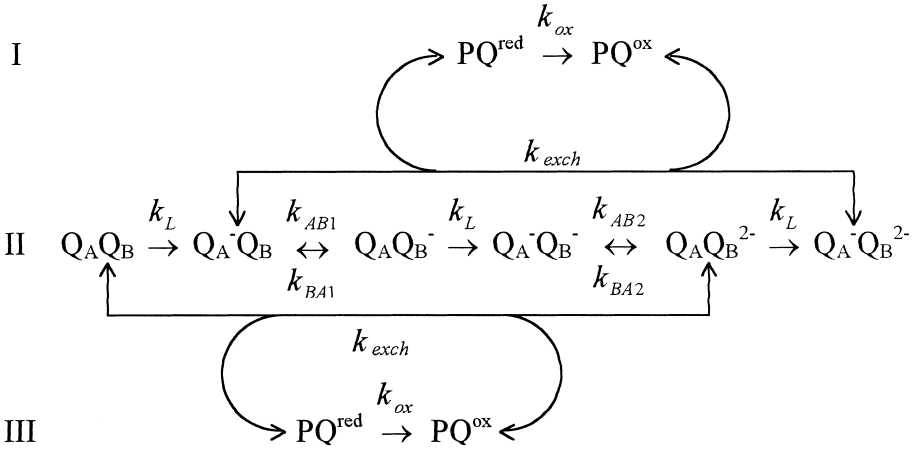

Fig. 5. A scheme of the two-electron gate model (row II) which describes that Q_B, unlike Q_A, accepts two electrons sequentially. k_L is the rate of Q_A reduction, k_{AB1} and k_{AB2} are the forward rate constants for the electron transport from Q_A^- to Q_B and from Q_A^- to Q_B^-, respectively, whereas k_{BA1} and k_{BA2} are the rate constants for the back electron transport from Q_B^- to Q_A and from Q_B^{2-} to Q_A, respectively. Rows I and III describe an exchange of the doubly reduced Q_B (after its protonation) with an oxidised PQ molecule from the PQ pool with the rate constant k_{exch}, and the oxidation of the reduced PQ pool by cytochrome b_6/f complex with the rate constant k_{ox}. The reactions described by the rate constant k_{exch} are reversible with an equilibrium constant equals 1 [205] and thus the value of k_{exch} represents the values of forward and also backward rate constants for these reactions. For the values of the rate constants, see Table 1.

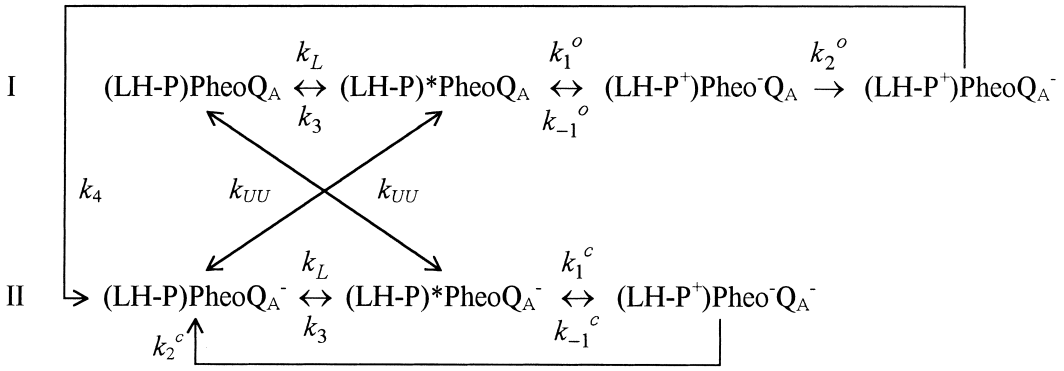

Fig. 6. A scheme of the RRP model. LH denotes all the light harvesting antenna of PS II, P and Pheo denote P680 and pheophytin, respectively. (LH-P)* represents all the pigments (from the antenna and P680) in the fast energy equilibrium of excited state. The fast equilibrium occurs when $\tau_{eq} \ll \tau_{mean}$, where τ_{eq} and τ_{mean} is a time necessary for equilibrium and an average lifetime of excitons, respectively (see [239]). It was theoretically computed that for PS II, $\tau_{eq} = 26$ ps and $\tau_{mean} = 132$ ps [49]. Superscripts − or + denote the reduced or oxidised form. k_1^o, k_{-1}^o, k_2^o is the overall rate constant for charge separation, the rate constant for charge recombination and the rate constant for charge stabilisation in the open RC II. The charge stabilisation is considered to be an irreversible reaction which is in agreement with the estimation of a very high equilibrium constant for the reaction $Pheo^- Q_A \leftrightarrow PheoQ_A^-$ to be about $4–8 \times 10^5$ [289,290]. The overall rate constant for charge separation and rate constant for charge recombination in closed RC II are denoted as k_1^c, k_{-1}^c, respectively, and k_2^c is the rate constant for the non-radiative charge recombination to the ground state in closed RC II. The overall rate constants for charge separations $k_1^{o(c)}$ are related to the intrinsic rate constants of charge separation $k_{1,int}^{o(c)}$ (under the assumption of a spectrally homogenous antenna complexes of PS II) by $k_{1,int}^{o(c)} = N\, k_1^{o(c)}$, where N is the number of pigments in all the antenna complexes of PS II (which are in fast equilibrium with P680) [239]. The energy transfer between the closed and the open RC IIs is expressed by the rate constant k_{UU}. The rate constants of the deactivation of excited states through heat dissipation or emission as fluorescence in the open (k_3^o) and the closed RC IIs (k_3^c) are assumed to be equal, thus $k_3^o = k_3^c = k_3$. The equality is also assumed for the rates of exciton formation in the light harvesting antenna complexes in the open (k_L^o) and the closed RC IIs (k_L^c) expressed by $k_L^o = k_L^c = k_L$. k_4 is the rate constant for $P680^+$ reduction by Y_Z (tens–hundreds microseconds) or by the S-state transitions (tens microseconds–millisecond). For the values of the rate constants, see Table 1. This scheme can also be used for an explanation of the PSU models even if there are missing other electron acceptors over Q_A in the scheme (i.e., Q_B and PQ pool) which form complete PS II. When the model of separate PSUs is assumed, the photosynthetic apparatus (all PS IIs in the sample) can be described by two possible states: the open PSUs, the light reactions of which are described in row I and the closed PSUs, the light reactions of which are described in row II. In the model of separate PSUs, the overall rate constant k_{UU} for the excitation energy transfer between the closed and open PSUs is zero. In the case of the assumption of the statistical model of PSU, the photosynthetic apparatus can be hypothetically described by one PSU within which the reactions in rows I and II occur and k_{UU} is infinite. For the model of connected PSUs, it is assumed that the photosynthetic apparatus can be described in the same way as the separated PSUs but k_{UU} has non-zero value. When the domain structure is assumed, the photosynthetic apparatus is arranged into the domains where one domain is considered as the statistical PSU but all the domains are separated as for the energy transfer.

types of arrangement of the photosynthetic apparatus. The combination of the separate PSU model and statistical model leads to an arrangement of the photosynthetic apparatus into domains where there can be a finite or hypothetically infinite number of P680s in one big reservoir of antenna pigments in one domain [92,297–299]. The excitation energy transfer is not restricted within one domain (the statistical model for one domain) but cannot proceed between domains (the domains are separated). On the other hand, when the photosynthetic apparatus is arranged into separated PSUs but excitation energy transfer between these PSUs can occur in some way, then we have the model of connected PSUs [52,78,165,300–305]. For an explanation of the difference between particular PSU models see Fig. 6.

There is no agreement in the literature as to which model is a true representation of the photosynthetic system but the latest theoretical simulations and fitting of experimental data tend to select the model of connected PSUs [63,64,95,132,263,264,332,333]. On the other hand, for PS II core particles, the best agreement of the experimental data was found for the domain arrangement of PS II [109].

Excitation energy transfer within one PSU (not

Table 1
The values of the rate constants involved in the two-electron gate model (Fig. 5) and the RRP model (Fig. 6)

Rate constants	Values in s^{-1}	Notes and references
$k^{o}_{1,int}$	$\approx 4\times10^{11}$	[16,22,237,238,240–245]
$k^{c}_{1,int}$	$6–10\times10^{10}$	[22,237,238]
k^{o}_{1}	$1.9–9.3\times10^{9}$	[22,237,238]
k^{o}_{-1}	$0.3–2\times10^{9}$	[22,237,238]
k^{o}_{2}	$2–2.3\times10^{9}$	[22,237,238]
k^{c}_{1}	$0.47–1.5\times10^{9}$	[22,237,238]
k^{c}_{-1}	$0.23–3.3\times10^{9}$	[22,237,238]
k^{c}_{2}	$0.3–1\times10^{9}$	[22,237,238]
k_3	$0.25–1\times10^{9}$	[22,237,238,246–249]
k_4	$3.8–50\times10^{6}$	$P680^{+}$ reduction by Y_Z, [250,251]
	$0.667–33.3\times10^{3}$	S-state transitions of OEC, [252–262]
k_L	≈ 5500	For ≈ 3000 μmol m^{-2} s^{-1}, [333]
k_{UU}	$1–6\times10^{9}$	For higher plants, [63,64]
	$3.5–42\times10^{9}$	For purple bacteria, [263,264]
k_{AB1}	$2.5–5\times10^{3}$	[66,265–273]
k_{BA1}	≈ 175	For $K_{AB1/BA1}=20$, [80,268,274,275]
k_{AB2}	$1.25–3.33\times10^{3}$	[66,265–273]
k_{BA2}	≈ 35	For $K_{AB2/BA2}=50$, [274,276,277]
	Same as k_{AB2}	For $K_{AB2/BA2}=1$, [275]
k_{exch}	$0.12–1\times10^{3}$	For 'fast' PQ pool, [272,278–283]
	3–8	For 'slow' PQ pool, [282,283]
k_{ox}	50–500	[281,284–288]

$K_{AB1/BA1}$ and $K_{AB2/BA2}$ are the equilibrium constants for the forward and backward electron transports between Q_A^- and Q_B and between Q_A^- and Q_B^-, respectively.

dependent on the type of PSU) can also be described by many model approaches which treat different aspects of excitation energy transfer. The models are: homogeneous lattice, funnel model, pebble-mosaic model, monopartite, bipartite and tripartite models, and the (extended) RRP model (see Fig. 6). A thorough discussion of the models is in [239].

6.2. Fluorescence intensity dependence on state of Photosystem II

Utilisation of excitation energy for photochemistry in PS II leads to the formation of $P680^{+}Q_A^-$. After the electron donation from the donor side of PS II, the $P680Q_A^-$ is formed which, after its excitation, is transformed to the $P680^{*}Q_A^-$. As it has been suggested that there is no direct fluorescence emission of this form [306], the exciton is rapidly transferred back to the antenna pigments of PS II where it is emitted as fluorescence. Thus, it was originally supposed by Duysens and Sweers [65] that the fluorescence intensity during FI can be expressed as a function of the amount of closed RC II (Q_A reduced). When Pheo was discovered as the first electron acceptor in PS II by Klimov et al. [307], it was suggested that the fluorescence of photosynthetic apparatus is a nanosecond luminescence originating from the charge recombination between a $P680^{+}$ and $Pheo^{-}$ [307–309] leading to the excited state of the P680 which then transfers excitation energy to the antenna complexes of PS II as in the previous hypothesis. This mechanism is, according to Breton [310], responsible for fluorescence emission at 685 nm. The author even hypothesised that fluorescence emission at 695 nm originates from the direct luminescence of Pheo* which is formed by the charge recombination between the $P680^{+}$ and $Pheo^{-}$ [311]. However, the description of fluorescence emission from photosynthetic apparatus only as a nanosecond luminescence seems to be incorrect as concluded from more exact fluorescence measurements (see for reviews [239,312]). The RRP model (see Fig. 6) where P680, Pheo, Q_A and also the antenna pigments are involved, best describes the structure and function of RC II and also all fluorescence measurements. Recently, based on the RRP model it has been hypothesised that variable fluorescence during the course of FI can result from both prompt and also recombination fluorescence and that the yield of recombination fluorescence is modulated by non-radiative energy loss processes in RC II [313]. However, in the RRP model, the fluorescence intensity changes during FI are also described as a function of the amount of reduced Q_A [63,64,132] as mentioned above. What follows below is a mathematical description of the fluorescence intensity during FI that is dependent on the amount of reduced Q_A and on the excitation energy transfer between/within PSUs leading to the sigmoidal course of FI.

A non-linear relationship between fluorescence intensity and the number of Q_A^- has been well-known for a long time. Paillotin derived [304,314] that the fluorescence intensity $F(t)$ at time t can be expressed as follows:

$$\frac{F(t)-F_0}{F_M-F_0}=\frac{(1-P)e'}{1-Pe'}, \quad (1)$$

where e' is a relative amount of reduced Q_A (between 0 and 1; function of time t) and $P = p(1-F_0/F_M)$. The left side of Eq. 1 is the relative variable fluorescence and goes from 0 to 1. There are two different processes hidden in the P parameter (no connection with the P step in FI). The first process is a competition between individual RC IIs for exciton capture for the charge separation expressed by the F_0/F_M parameter and the second process is the probability of excitation energy transfer from closed RC II (Q_A reduced) to another RC II expressed by the p parameter. This probability can be expressed as $p = k_{UU}/(k_{UU}+k_F+k_H+k_{Pcl})$, where k_{UU} is the rate constant for exciton transfer from RC II in one PSU to RC II in a neighbouring PSU and k_F, k_H and k_{Pcl} are rate constants of fluorescence, the non-radiative quenching of excitation energy, and the capture frequency of photochemistry in a PSU with closed RC II, respectively.

The p probability can be equal to one of three possible values. If $p = 0$ (the model of separated PSUs) then it can be derived from Paillotin's equation that the fluorescence intensity is proportional to the number of reduced Q_A as was supposed in an early stage of FI research [65,82,117]. On the other hand, for the statistical model where $p = 1$, Paillotin's equation has the form:

$$\frac{F(t)-F_0}{F_M-F_0} = \frac{(1-\frac{F_V}{F_M})e'}{1-\frac{F_V}{F_M}e'} \tag{2}$$

which it is possible to rewrite as:

$$F(t) = \frac{F_0}{1-e'\frac{F_V}{F_M}} \tag{3}$$

which was originally derived by Vredenberg and Duysens [295,296]. If $0 < p < 1$ then Paillotin's equation describes the connected PSUs. Moreover, under the assumption that the maximal quantum yield of PS II photochemistry ($1-F_0/F_M = F_V/F_M$) in connected PSUs equals 1 (i.e., $F_0 = 0$; however, practically impossible), the fluorescence intensity $F(t)$ at time t can be described by:

$$\frac{F(t)-F_0}{F_M-F_0} = \frac{(1-p)e'}{1-pe'}, \tag{4}$$

which is used very often. A formally identical equation was also suggested by Valkunas et al. [94] on the basis of the double hit model derived for the PAP measurements of FI. But Eq. 4 was first derived by Joliot and Joliot [300,301] as:

$$\frac{F(t)-F_0}{F_M-F_0} = k'I\frac{e'}{1-pe'}, \tag{5}$$

where k' is a constant (proportional to the rate constant of fluorescence) and I is the (relative) intensity of excited light.

As the fluorescence intensity goes from F_0 to F_M, Sorokin [93] included a new variable e'_M, the maximal relative amount of reduced Q_A when DCMU is applied, and suggested for the statistical model the following equation:

$$\frac{F(t)-F_0}{F_M-F_0} = \frac{(1-\frac{F_V}{F_M}e'_M)e'}{1-\frac{F_V}{F_M}e'_Me'}. \tag{6}$$

Assuming three main types of PSUs (small, big, and grouped, in his terminology), Strasser [315,316] suggested the grouping model and derived the following equation:

$$\frac{F(t)-F_0}{F_M-F_0} = \frac{e'}{1+p_{St}\frac{F_V}{F_0}(1-e')}, \tag{7}$$

where

$$p_{St} = \frac{p}{1+(1-p)\frac{F_V}{F_0}}. \tag{8}$$

Generally, the time dependence of fluorescence intensity can be summarised by the equation [317]:

$$\frac{F(t)-F_0}{F_M-F_0} = \frac{e'}{1+c(1-e')} \tag{9}$$

where the constant c equals:

$$c_P = \frac{p\frac{F_V}{F_M}}{1-p\frac{F_V}{F_M}} \tag{10}$$

according to the model of Paillotin [304,314],

$$c_{VD} = \frac{\frac{F_V}{F_M}}{1-\frac{F_V}{F_M}} \quad (11)$$

according to the model of Vredenberg and Duysens [295,296],

$$c_J = \frac{p}{1-p} \quad (12)$$

according to the model of Joliot and Joliot [300, 301],

$$c_{So} = \frac{\frac{F_V}{F_M}e'_M}{1-\frac{F_V}{F_M}e'_M} \quad (13)$$

according to the model of Sorokin [93], and

$$c_{St} = p_{St}\frac{F_V}{F_0} = \frac{p}{\frac{F_M}{F_V}-p} \quad (14)$$

according to the model of Strasser [315,316].

The parameter c_J is usually denoted as J (no connection with the J step in FI) and was found to be a function of the rate constants in PS II [95]. The dependence of the J parameter on these PS II parameters was further derived on the basis of the RRP model for the connected PSUs [63,64], the connected PSUs with a heterogeneous antenna and the statistical model of PSUs [63].

It is clear from the above that the sigmoidicity is caused by the non-zero probability that an exciton visiting a closed RC II can visit another RC II. Depending on the used model for PSUs, this probability may be a function of the trapping properties of the closed RC II or the connective properties of PSUs or both. In the case of the statistical model of the PSU [295,296] which assumes $p = 1$ (i.e., energetic communication within PSU without any restriction), the sigmoidicity is only caused by the F_V/F_M parameter (the trapping properties of the closed RC II; Eqs. 2 and 3). This was also confirmed by simulations performed in [6]. Using this approach, the F_V/F_M parameter was found to be about 0.65 [80]. An extensive discussion on the relationship between F_V/F_M parameter and the sigmoidicity of FI was performed in [92,94]. However, according to [93], assuming the statistical model of the PSU, the sigmoidicity is, in addition to the F_V/F_M parameter, affected by the value of the e'_M parameter (higher e'_M, larger sigmoidicity, Eq. 6). On the other hand, when energetic communication between PSUs is somehow restricted as in the model of connected PSUs, both the F_V/F_M and p parameters are responsible for the sigmoidicity (both the trapping properties of the closed RC II and the connective properties of PSUs; Eqs. 1,7,8). When F_V/F_M is assumed to equal 1 (i.e., $F_0 = 0$; however, practically impossible) in the model of connected PSUs, the sigmoidicity is only caused by a restricted energetic communication between PSUs determined by $p < 1$ (the connective properties of PSUs; Eqs. 4 and 5). Under this assumption the value of p was found to be about 0.55 [300] and about 0.75 assuming two types of connected PSUs, the second with its antenna twice as large as the first [301]. As it is well known that the F_V/F_M parameter has a value about 0.83 [69], it is interesting that using the statistical model a smaller value (0.65) was found [80] and on the other hand, a higher value (1) is assumed in the Joliots' derivation of the model of the connected PSUs [300,301]. As the direct measurements and theoretical estimates for the quantum yield of charge separation and stabilisation lead to values of 1 and 0.9, respectively [55,88,89], the model of connected PSUs seems to be more appropriate. But because there is more than one process hidden in the sigmoidicity of FI, it is probably not correct to use Eq. 2 when the statistical model of PSUs is not guaranteed. Similarly, Eq. 4 should not be used when one cannot guarantee that F_V/F_M equals 1. However, the equation derived by Paillotin is probably the best description of the real situation because it considers the trapping properties of the closed RC II and also the connective properties of PSUs. Also more detailed expressions derived on the basis of the RRP model applied to the model of connected PSUs supported Paillotin's equation [63].

Even if it is clear from the text above that the energy transfer between/within PSUs exists, there is an agreement in the literature that when $p \leq 1/3$, FI is more nearly exponential (concave) than sigmoidal in shape [92,183,304], and when $p \leq 0.15$, FI can be well approximated by an exponential rise [101]. On the other hand, it was derived that under the assumption of the statistical model of PSU, an expo-

nential increase of fluorescence intensity can be obtained for $e'_M < 1/3$ (see Eq. 6) [93].

The meaning of the p parameter was refined in regard of the islet effect proposed by Lavorel and Joliot [52]. The islet is created when two and more PS IIs with closed RC IIs (i.e., PS IIs which emit fluorescence) are formed side by side. The aggregation of fluorescing PS IIs into the islet can be random (in the case of separated PSUs) or active (in the case of connected PSUs). The active islet formation leads to a slower increase in fluorescence intensity in time than in the case of random islet formation. The difference between the increase in fluorescence intensity under active islet formation and random islet formation is more pronounced for high values of the p parameter and a high value of reduced Q_A [52]. The active islet formation can then lead to an underestimation of the p parameter determined from FI. Thus, the p parameter is usually calculated from the experimental data where the relative amount of reduced Q_A is smaller than 0.6 [305].

All equations mentioned above in this section express the dependence of fluorescence intensity on the number of reduced Q_A. But for practical reasons it is desirable to know the dependence of fluorescence intensity on time. Thus, it is necessary to find first a relationship between the number of reduced (or oxidised) Q_A and time. This relation was defined for the Joliots' connected PSUs (the assumption that $F_V/F_M = 1$) as follows [300]:

$$-\frac{de}{dt} = \frac{de'}{dt} = kI\frac{e}{1-pe'}, \tag{15}$$

where e ($= 1-e'$) is the number of oxidised Q_A and k is a constant (proportional to the rate constant for PS II photochemistry, i.e., Q_A reduction). Integration of this equation, with initial condition at zero time $e(0) = 1$, leads to:

$$-p + (1-p)\ln e + ep = -kIt \tag{16}$$

A plot of fluorescence intensity as a function of time can be obtained by a combination of Eq. 16 with Eq. 4, where e' is considered as a parameter which determines time (Eq. 16) and fluorescence intensity (Eq. 4), respectively.

As e' increases with increasing time of the FI measurement, there is an increase in the effective size of the antenna which serves the remaining oxidised Q_A, leading thus to an increasing rate of Q_A reduction with increasing time (amount of Q_A^-). On the other hand, an expression for the change of the amount of e' with time in the first-order reaction $e \rightarrow e'$ occurring with the rate constant k_L is defined as:

$$\frac{de'}{dt} = k_L e. \tag{17}$$

A comparison of Eq. 15 with Eq. 17 leads to Eq. 18 which expresses the rate of Q_A reduction (k_L) to be dependent on the number of reduced Q_A (e'):

$$k_L = \frac{kI}{1-pe'}. \tag{18}$$

The product kI in Eq. 18 means the initial (relative) rate of Q_A reduction for the light illumination used and which can be obtained from FI measured with DCMU. However, on the basis of the statistical model, where F_V/F_M (denoted as k_p) is used instead of p, there is one more k_p in the numerator of Eq. 18 (e.g. [80,87,318]). On the basis of the RRP model and the two-electron gate model for electron transport from Q_A to Q_B, the rate of Q_A reduction was precisely derived [132] being at any time a function of the amount of closed RC IIs.

All the above equations described the dependence of the fluorescence intensity on the number of closed RC II (Q_A is reduced). But as has been mentioned in Section 2, an accumulation of triplet states and annihilation processes can also significantly change the course of FI. Thus, here is a brief description of the theory of FI in relation to the singlet-triplet annihilation processes [115,116]. First, it is necessary to know the amount of singlet excitations in a domain, $n_{i,T}$, characterised by i closed RC IIs and T triplet excitations (no connection with the T step in FI). This amount is, in addition to i and T, a function of the relative rates for intersystem crossing and singlet–triplet quenching, and the excitation fluence J (no connection with the J step in FI). Then, the probability $P_{i,T}$ to find the domain under the selected conditions is defined by the recurrence formula. Fluorescence of the domain under the selected conditions is:

$$F_{i,T} = \frac{K_f n_{i,T}}{J} \tag{19}$$

where K_f is the fluorescence rate and the course of fluorescence during FI is then expressed as follows:

$$F = \sum_i P_{i,T}\ F_{i,T} \tag{20}$$

6.3. Results of the mathematical modelling of fluorescence induction

On the basis of the known structural models of PS II and the theory of FI, FI has been simulated or theoretical models fitted to experimental FI data. Such simulations or fitting are of great importance in photosynthesis research because one can obtain a great deal of information about the kinetics and structure of PS II. Thus, the most important results are briefly described and discussed below. But first it is mentioned which model of PS II structure and definition of fluorescence during FI were used in specific cases.

When FI has been simulated or a theoretical model fitted to experimental FI data, some authors assumed that only 'slow' events described by the two-electron gate based model (Fig. 5) can sufficiently describe FI [54,133,168–173,318–320]. Others assumed that 'fast' events described by the RRP model (Fig. 6) can satisfactorily describe FI [6,63,64,332, 333]. In one case the authors considered both the two-electron gate based model and the RRP model in fitting experimental FI data [132].

Although fluorescence as such is exactly defined, different 'definitions' for fluorescence during FI were used. They can be divided into 'amount dependent' and 'rate dependent' ones. The 'amount dependent' definition means that fluorescence is calculated with the help of the relative amount of Q_A^-, either directly (valid only for separated PSUs) [168,169,171,172] or using Eq. 4 or a similar expression [54,93,170,173, 318–320]. The 'rate dependent' definition means that fluorescence during FI is somehow computed with the help of the rate constant of fluorescence, that is as $F(t) = k_F/k_F+k_D+k_P\ [Q_A]$ (k_F, k_D and k_P are the rate constants of fluorescence, internal energy conversion and photochemistry, respectively, and $[Q_A]$ is the amount of open RC IIs) [133] or as a radiative decay of the excited states to the ground state (via k_F) [132,333] or as a time integral (from zero to infinity) of the excited states (involving k_F) [6,63,64,332].

Except for the works of Lazár et al. and Stirbet et al. [54,168–173,320,333] where a simulation of FI measured under high light illumination was done, other researchers [6,63,64,93,132,133,318,319,332] dealt with simulation or fitting of FI measured under low light illumination. Simulations of FI measured by PAP techniques were done in [92,115,116].

Hsu [318] and Renger and Schulze [319] described FI measured under low light illumination with the help of the two-electron gate model up to the exchange of doubly reduced Q_B with a PQ molecule from the pool. While in [319] the authors found that it is only possible to fit the experimental FI when there is an exponential decrease in the rate of exchange of doubly reduced Q_B with PQ from the pool with an increasing time period of measurements, in [318] the author found that the addition of more particular FI curves is necessary to obtain a final successful simulation of FI. The particular FI curves in the sum differ in the assumed number of PQ molecules in the PQ pool used in the particular simulation. As discussed by Hsu [318], the assumed different number of PQ molecules in the pool is probably an expression of the same case as the exponential decrease in the rate of Q_B^{2-} exchange used in [319]. There may in fact be two PQ pools which differ in the rate of their reduction as was suggested in [39,101,179] and found in [282,283].

The two-electron gate mechanism was also used by Goltsev and Yordanov [133] for their simulation of FI measured under low light illumination. The authors also considered a proton gradient across the thylakoid membrane originating from the electron transport in their model. Although the time course of the simulated FI was in close agreement with the experimental data, the values of the rate constants used are far (one to two orders) from the generally accepted ones.

Sorokin [93] simulated the course of FI measured with DCMU under low light illumination. The author suggested that a new parameter e'_M (the maximal amount of reduced Q_A when DCMU is applied) is essential for a description of the course of FI (see previous subsection). As e'_M is intensity dependent (higher intensity of light, higher e'_M) variation in this parameter can lead, even under the assumption

of the statistical model of PSU (energetic communication within PSU without any restriction), to an exponential or sigmoidal course of FI measured with DCMU (higher e'_M, larger sigmoidicity).

Trissl et al. [6] simulated the time course of FI with the help of the RRP model and using three sets of the published rate constant [22,237,238]. Trissl et al. [6] assumed the statistical model for PSUs (energetic communication within PSU without any restriction) and obtained a sigmoidal course of FI, and thus supported the previous results [80,295,296,304]. Trissl et al. [6] obtained results which contradicted the previous theory of FI and led to publication of critical letters on this problem [1,321,322]. Even though some results had numerical errors [323] most of them were correct and were further confirmed by Lavergne and Trissl [63,64]. These authors applied the RRP model to the statistical model of PSUs, the connected PSUs and to the connected PSUs with a heterogeneous antenna system, and derived an analytical solution for the fluorescence intensity during the FI. Among other things, the authors found that F_0 and F_M are only functions of RC II parameters and do not depend on the excitation energy transfer between PSUs which is characterised by the J parameter (see previous subsection) introduced in [95]. Also, the CA over FI curve does not depend on the excitation energy transfer. Up to the time of this review, the work of Lavergne and Trissl [63,64] is the most detailed analysis of the theory of FI and, it was further used in [109,263,264]. The model of Lavergne and Trissl has been modified by Vavilin et al. [332] by assuming in addition the presence of photoinhibited PS IIs which do not trap excitons for photochemistry but efficiently dissipate the absorbed light energy. These authors have concluded that there is excitation energy transfer between photoinhibited and active PS IIs and that photoinhibition lowers the yield of radical pair formation in remaining active PS IIs [332].

A conjunction of 'slow' events with 'fast' events in PS II for the description of FI measured under low light illumination was made in [132] based on an earlier short report [324]. The main importance of this work is that the authors [132] found an exact expression for the rate of Q_A reduction in the slow model (the two-electron gate model) which is based on 'fast' events (the RRP model). These authors found that their theoretical model can be very well fitted to the experimental FI even for both contradictory values of the equilibrium constant $K_{AB2/BA2}$ for the electron transport between Q_A^- and Q_B^- which was found to be 50 [274,276,277] or 1 [275] (see Fig. 5 and Table 1). Baake and Schlöder [132] explained it to be a consequence of using both 'slow' and 'fast' events for the description of FI leading to a relation between the particular parameters of slow and fast events. These authors further tried to improve their model by considering the Q_B-nonreducing RC II, the quenching of fluorescence by the oxidised PQ pool (see Section 2), a detailed scheme for the protonation of the double reduced Q_B, and a detailed scheme for the oxidation of the reduced PQ pool by PS I. However, these approaches did not lead to a better agreement between the theoretical and experimental FIs and sometimes unrealistic results were obtained (negative values of the rate constants).

The accumulation of particular redox forms of Q_A and Q_B which were obtained from the simulation and fitting of the time course of FI measured under low light illumination is described in Section 2.

FI measured under high light illumination was first simulated on the basis of the two-electron gate model by Stirbet and Strasser [168], presented also in [169,171]. Excepting that these authors assumed that fluorescence intensity is directly proportional to the amount of Q_A^- (valid only for separate PSUs), the main weakness of this work was the use of an unknown component X accepting electrons faster than the electron transport in the main electron chain (the two-electron gate). This weak point can be also found in [54,172]. However, the authors simulated the FI curve with the typical O–J–I–P pattern. An improved version of the simulation was presented in [170] where the previous weakness was eliminated. The authors found that the increase in the rate constant for the oxidation of reduced PQ pool leads to a local decrease in fluorescence intensity to a dip after the J step whereby they confirmed the origin of the decrease in fluorescence intensity (before the P step is reached) to be due a dynamic equilibrium between PS II and PS I [47,130].

Three different types of PS II were considered in the simulation of FI measured under high light illumination by Lazár et al. [54]. To obtain the usual value of the F_V/F_M parameter, the authors consid-

ered in addition to the Q_B-reducing and Q_B-nonreducing RC IIs, in their terminology, inactive RC IIs (12% of all RC IIs) which are always closed even in darkness. In their model, the authors better distinguished the Q_B-reducing RC II from the Q_B-nonreducing RC II than in the previous cited papers, and assumed that the rates of Q_A reduction are driven by the slowest events in the electron transport in RC II which are the S-state transitions of OEC.

The influence of PS II heterogeneity and a state of OEC on the course of FI measured under high light illumination were further examined by Strasser and Stirbet [320] and Stirbet et al. [173], respectively. In [320] the authors have found that the course of FI simulated for PS IIα and PS IIβ (all of Q_B-reducing type) can be well approximated by the course of FI simulated for only one type of PS II characterised by an average antenna size and connectivity parameter. But no 'average PS II' can describe the course of FI simulated for a photosynthetic apparatus where some Q_B-nonreducing RC IIs are present [320]. A detailed description of OEC function (S-state transitions) together with a description of the acceptor side of PS II was for the first time used for simulation of FI measured under high light illumination by Stirbet et al. [173]. The authors discussed in detail how changes in some PS II parameters (rate constants, number and initial ratio of some components in PS II, connectivity between PS IIs) affect the FI. Among other things, the authors have suggested that a decrease in fluorescence intensity to a local minimum (dip) after the I step is mainly caused by OEC function; however, the appearance of the dip is also influenced by many other factors [173].

Lazár and Pospíšil [333] have used the RRP model firstly extended by detailed description of the donor side of PS II (i.e. electron donation from Y_Z to $P680^+$ and subsequent electron donation from the S-state transitions of OEC to Y_Z^+) for simulations of FI, measured at room and high temperatures in the presence of DCMV. The authors have shown that assumption of inhibition of the S-state transitions of OEC in their extended RRP model results in simulation of FI which perfectly fits the experimental FI measured with DCMV at high temperature where inhibition of OEC has been suggested [197–200]. On the other hand, assumption of full function of OEC in the extended RRP model leads to simulation of FI which perfectly agrees with the experimental FI measured with DCMV at room temperature [333].

Practically the same results were obtained in all papers dealing with the simulation of FI measured under high light illumination as for an accumulation of particular redox forms of Q_A and Q_B in particular steps of the FI as it is mentioned in Section 3.

A theory of singlet–triplet annihilation has been described for the lake model with an infinite number of RC II [115] and for a domain structure of a PSU with up to 4 RC IIs in the domain [116]. The effect of the singlet–triplet annihilation on the sigmoidicity of FI was evident for both the lake model of PSU, as well as the domain structure of PSU. However, it has been suggested [116] that consideration of the singlet–triplet annihilation within the lake model of PSU is incorrect because the action radius of the triplets is limited by the finite size of PSU. A similar conclusion was also theoretically demonstrated in [92]: when annihilation processes are considered in a domain of more than 3 RC IIs, there is no fluorescence rise in FI due to the annihilation processes.

Acknowledgements

I would like to thank J. Nauš for his critical reading of the manuscript, J. Lavergne for his critical reading and suggestions for Subsection 6.2, and M. Havaux, R.J. Strasser, and L. Valkunas for the experimental data for Fig. 3A, Fig. 3B curve c, and for Fig. 4, respectively.

References

[1] A.R. Holzwarth, Biophys. J. 64 (1993) 1280–1281.
[2] P. Latimer, T.T. Bannister, E. Rabinowitch, Science 124 (1956) 585–586.
[3] A. Müller, R. Lumry, M.S. Walker, Photochem. Photobiol. 9 (1969) 113–126.
[4] R. Avarmaa, T. Soovik, A. Tamkivi, B. Tonissoo, Studia Biophys. Berlin 65 (1977) 213–218.
[5] A. Pfarrherr, K. Tencher, D. Leupold, P. Hoffmann, J. Photochem. Photobiol. B: Biol. 9 (1991) 35–41.
[6] H.-W. Trissl, Y. Gao, K. Wulf, Biophys. J. 64 (1993) 974–988.

[7] H.J.K. Keuper, K. Sauer, Photosynth. Res. 20 (1989) 85–103.
[8] J.B. Marder, V.I. Raskin, Photosynthetica 28 (1993) 243–248.
[9] A.M. Gilmore, T.L. Hazlett, P.G. Debrunner, Govindjee, Photosynth. Res., 48 (1996) 171–187.
[10] J.-M. Briantais, J. Dacosta, Y. Goulas, J.-M. Ducruet, I. Moya, Photosynth. Res. 48 (1996) 189–196.
[11] O. Namba, K. Satoh, Proc. Natl. Acad. Sci. USA 84 (1987) 109–112.
[12] M. Kobayashi, H. Maeda, T. Watanabe, H. Nakatane, K. Satoh, FEBS Lett. 260 (1990) 138–140.
[13] K. Gounaris, D.J. Chapman, P. Booth, B. Crystall, L.B. Giorgi, D.R. Klug, G. Porter, J. Barber, FEBS Lett. 265 (1990) 88–92.
[14] P.J. van Leeuwen, M.C. Nieveen, E.J. van de Meent, J.P. Dekker, H.J. van Gorkom, Photosynth. Res. 28 (1991) 149–153.
[15] G. Chumanov, R. Picorel, S. Toon, M. Seibert, T.M. Cotton, Photochem. Photobiol. 58 (1993) 757–760.
[16] A.R. Holzwarth, M.G. Müller, G. Gatzen, M. Hucke, K. Griebenow, J. Luminesc. 60/61 (1994) 497–502.
[17] C. Eijckelhoff, J.P. Dekker, Biochim. Biophys. Acta 1231 (1995) 21–28.
[18] K. Akabori, H. Tsukamoto, J. Tsukihara, T. Nagatsuka, O. Motokawa, Y. Toyoshima, Biochim. Biophys. Acta 932 (1988) 334–357.
[19] G. Paillotin, J. Theor. Biol. 58 (1976) 219–235.
[20] G.H. Krause, E. Weis, Annu. Rev. Plant Physiol. Plant Mol. Biol. 42 (1991) 313–349.
[21] D. Wong, Govindjee, FEBS Lett., 97 (1979) 373–377.
[22] T.A. Roelofs, Ch.-H. Lee, A.R. Holzwarth, Biophys. J. 61 (1992) 1147–1163.
[23] H. Kautsky, A. Hirsch, Naturwissenschaften 19 (1931) 964.
[24] H.K. Lichtenthaler, Photosynthetica 27 (1992) 45–55.
[25] Govindjee, Aust. J. Plant. Physiol., 22 (1995) 131–160.
[26] J. Franck, Annu. Rev. Plant Physiol. 2 (1951) 53–86.
[27] E.C. Wassink, Adv. Enzymol. 11 (1951) 91–199.
[28] E.I. Rabinowitch, in: Photosynthesis and Related Processes, vol. II, Part 1, Wiley Interscience, New York, 1951, pp. 603–1208.
[29] E.I. Rabinowitch, in: Photosynthesis and Related Processes, vol. II, Part 2, Wiley Interscience, New York, 1956, pp. 1211–2088.
[30] L.N.M. Duysens, in: Govindjee, J. Amesz, D.C. Fork (Eds.), Light Emission by Plants and Bacteria, Academic Press, New York, 1986, pp. 3–28.
[31] G.H. Mohammed, W.D. Binder, S.L. Gillies, Scand. J. For. Res. 10 (1995) 383–410.
[32] G. Papageorgiou, in: Govindjee (Ed.), Bioenergetics of Photosynthesis, Academic Press, New York, 1975, pp. 319–366.
[33] J. Lavorel, A.-L. Etienne, in: J. Barber (Ed.), Primary Processes of Photosynthesis Elsevier, Amsterdam, 1977, pp. 203–268.
[34] G.H. Krause, E. Weis, Photosynth. Res. 5 (1984) 139–157.
[35] Govindjee, K. Satoh, in: Govindjee, J. Amesz, D.C. Fork (Eds.), Light Emission by Plants and Bacteria, Academic Press, New York, 1986, pp. 497–537.
[36] G. Renger, U. Schreiber, in: Govindjee, J. Amesz, D.C. Fork (Eds.), Light Emission by Plants and Bacteria, Academic Press, New York, 1986, pp. 587–619.
[37] J.-M. Briantais, C. Vernotte, G.H. Krause, E. Weis, in: Govindjee, J. Amesz, D.C. Fork (Eds.), Light Emission by Plants and Bacteria, Academic Press, New York, 1986, pp. 539–583.
[38] O. van Kooten, F.H. Snel, Photosynth. Res. 25 (1990) 147–150.
[39] R.J. Strasser, A. Srivastava, Govindjee, Photochem. Photobiol., 61(1) (1995) 32–42.
[40] M.J. Joshi, P. Mohanty, J. Sci. Ind. Res. 54 (1995) 155–174.
[41] G.C. Papageorgiou, J. Sci. Ind. Res. 55 (1996) 596–617.
[42] J. Lavorel, Plant Physiol. 34 (1959) 204–209.
[43] J. Lavorel, Colloques Internationaux du Centre National de la Recherche Scientifique 119 (1963) 161–176. (in French)
[44] E. Ögren, Planta 175 (1988) 229–236.
[45] W.L. Butler, in: A. Trebst, M. Avron (Eds.), Encyclopedia of Plant Physiology. Photosynthesis I vol. 5, Springer, Berlin, 1977, pp. 149–167.
[46] W.L. Butler, Annu. Rev. Plant Physiol. 29 (1978) 345–378.
[47] J.C.M. Munday, Govindjee, Biophys. J., 9 (1969) 1–21.
[48] P. Mathis, G. Paillotin, in: M.D. Hatch, N.K. Boardman (Eds.), The Biochemistry of Plants, vol. 8, Academic Press, New York, 1981, pp. 97–161.
[49] P.D. Laible, W. Zipfel, T.G. Owens, Biophys. J. 66 (1994) 844–860.
[50] T.G. Owens, in: N.R. Baker (Ed.), Photosynthesis and the Environment, Kluwer, Dordrecht, 1996, pp. 1–23.
[51] R.K. Clayton, Biophys. J. 9 (1969) 60–76.
[52] J. Lavorel, P. Joliot, Biophys. J. 12 (1972) 815–831.
[53] J.B. Marder, V. Caspi, V.I. Raskin, in: P. Mathis (Ed.), Photosynthesis: From Light to Biosphere, vol. III, Kluwer, Dordrecht, 1995, pp. 305–308.
[54] D. Lazár, J. Nauš, M. Matoušková, M. Flašarová, Pestic. Biochem. Physiol. 57 (1997) 200–210.
[55] M.-L. Groot, R. van Grondelle, J.-A. Leegwater, F. van Mourik, J. Phys. Chem. B 101 (1997) 7869–7873.
[56] A.K. Mattoo, M. Edelman, Proc. Natl. Acad. Sci. USA 84 (1987) 1497–1501.
[57] J.E. Guenther, A. Melis, Photosynth. Res. 23 (1990) 105–109.
[58] L.A. Tumerman, E.M. Sorokin, Mol. Biol. 1 (1967) 628–638.
[59] R.K. Clayton, J. Theor. Biol. 14 (1967) 173–186.
[60] J.-M. Briantais, H. Markelo, Govindjee, Photosynthetica, 6 (1972) 133–141.
[61] M. Kitajama, W.L. Butler, Biochim. Biophys. Acta 376 (1975) 105–115.
[62] M. Havaux, Plant Sci. 94 (1993) 19–33.
[63] J. Lavergne, H.-W. Trissl, Biophys. J. 68 (1995) 2474–2492.
[64] H.-W. Trissl, J. Lavergne, Aust. J. Plant Physiol. 22 (1995) 183–193.

[65] L.N.M. Duysens, H.E. Sweers, in: Japanese Society of Plant Physiologists (Ed.), Studies on Microalgae and Photosynthetic Bacteria, University of Tokyo Press, Tokyo, 1963, pp. 353–372.
[66] B. Forbush, B. Kok, Biochim. Biophys. Acta 162 (1968) 243–253.
[67] U. Schreiber, Photosynth. Res. 9 (1986) 261–272.
[68] Ch. Neubauer, U. Schreiber, Z. Naturforsch. 42c (1987) 1246–1254.
[69] O. Björkman, B. Demmig, Planta 170 (1987) 489–504.
[70] B. Genty, J.-M. Briantais, N.R. Baker, Biochim. Biophys. Acta 990 (1989) 87–92.
[71] R. van Grondelle, Biochim. Biophys. Acta 811 (1985) 147–195.
[72] D. Lazár, J. Nauš, Photosynthetica 35 (1998) 121–127.
[73] J.C.M. Munday, Govindjee, Biophys. J., 9 (1969) 22-35.
[74] W. Oettmeier, H.J. Soll, Biochim. Biophys. Acta 724 (1983) 287–297.
[75] A. Trebst, W. Draber, Photosynth. Res. 10 (1986) 381–392.
[76] A. Trebst, Z. Naturforsch. 42C (1987) 742–750.
[77] Y. Shigematsu, F. Satoh, Y. Yamada, Pestic. Biochem. Physiol. 35 (1989) 33–41.
[78] W.W. Doschek, B. Kok, Biophys. J. 12 (1972) 832–838.
[79] P. Bennoun, Y.-S. Li, Biochim. Biophys. Acta 292 (1973) 162–168.
[80] A. Melis, L.N.M. Duysens, Photochem. Photobiol. 29 (1979) 373–382.
[81] N. Murata, M. Nishimura, A. Takamiya, Biochim. Biophys. Acta 120 (1966) 23–33.
[82] S. Malkin, K. Kok, Biochim. Biophys. Acta 126 (1966) 413–432.
[83] A. Melis, P.H. Homann, Photochem. Photobiol. 21 (1975) 431–437.
[84] A. Melis, P.H. Homann, Photochem. Photobiol. 23 (1976) 343–350.
[85] A. Melis, Biochim. Biophys. Acta 808 (1985) 334–342.
[86] S.W. McCauley, A. Melis, Photochem. Photobiol. 46 (1987) 543–550.
[87] A. Melis, U. Schreiber, Biochim. Biophys. Acta 547 (1979) 47–57.
[88] A.P.G.M. Thielen, H.J. van Gorkom, Biochim. Biophys. Acta 635 (1981) 111–120.
[89] A.P.G.M. Thielen, H.J. van Gorkom, Biochim. Biophys. Acta 637 (1981) 439–446.
[90] A. Melis, J.M. Anderson, Biochim. Biophys. Acta 724 (1983) 473–484.
[91] J.M. Anderson, A. Melis, Proc. Natl. Acad. Sci. USA 80 (1983) 745–749.
[92] W.T.F. Den Hollander, J.G.C. Bakker, R. van Grondelle, Biochim. Biophys. Acta 725 (1983) 492–507.
[93] E.M. Sorokin, Photobiochem. Photobiophys. 9 (1985) 3–19.
[94] L.L. Valkunas, N.E. Geacintov, L. France, J. Breton, Biophys. J. 59 (1991) 397–408.
[95] J. Lavergne, E. Leci, Photosynth. Res. 35 (1993) 323–343.
[96] D.H. Bell, M.F. Hipkins, Biochim. Biophys. Acta 807 (1985) 255–262.
[97] J. Sinclair, S.M. Spence, Biochim. Biophys. Acta 935 (1988) 184–194.
[98] J. Sinclair, S.M. Spence, Photosynth. Res. 24 (1990) 209–220.
[99] B.-D. Hsu, Y.-S. Lee, Y.-R. Jang, Biochim. Biophys. Acta 975 (1989) 44–49.
[100] B.-D. Hsu, Y.-S. Lee, Biochim. Biophys. Acta 1056 (1991) 285–292.
[101] P.C. Meunier, D.S. Bendall, Photosynth. Res. 32 (1992) 109–120.
[102] M.T. Black, T.H. Brearley, P. Horton, Photosynth. Res. 8 (1986) 193–207.
[103] Govindjee, Photosynth. Res., 25 (1990) 151–160.
[104] A. Melis, Biochim. Biophys. Acta 1058 (1991) 87–106.
[105] K.K. Karukstis, J. Photochem. Photobiol. B: Biol. 15 (1992) 63–74.
[106] J. Lavergne, J.-M. Briantais, in: D.R. Ort, Ch.F. Yocum (Eds.), Oxygenic Photosynthesis: The Light Reactions, Kluwer, Dordrecht, 1996, pp. 265–287.
[107] P. Morin, J. Chim. Phys. 61 (1964) 64–680.
[108] J. Lavorel, C.R. Acad. Sci. Paris 274D (1972) 2909–2912. in French
[109] P. Jahns, H.-W. Trissl, Biochim. Biophys. Acta 1318 (1997) 1–5.
[110] R.K. Clayton, Photochem. Photobiol. 5 (1966) 807–821.
[111] T.G. Monger, W.W. Parson, Biochim. Biophys. Acta 460 (1977) 393–407.
[112] J. Breton, N.E. Geacintov, C.E. Swenberg, Biochim. Biophys. Acta 548 (1979) 616–635.
[113] F. van Mourik, K.J. Visscher, J.M. Mulder, R. van Grondelle, Photochem. Photobiol. 57 (1993) 19–23.
[114] G. Denium, T.J. Aartsma, R. van Grondelle, J. Amesz, Biochim. Biophys. Acta 976 (1989) 63–69.
[115] V. Cervinskas, L. Valkunas, F. van Mourik, Lith. J. Phys. 34 (1994) 375–378.
[116] L. Valkunas, V. Cervinskas, F. van Mourik, J. Phys. Chem. B 101 (1997) 7327–7331.
[117] S. Malkin, Biochim. Biophys. Acta 126 (1966) 433–442.
[118] C. Vernotte, A.L. Etienne, J.-M. Briantais, Biochim. Biophys. Acta 545 (1979) 519–527.
[119] A.P.G.M. Thielen, H.J. van Gorkom, FEBS Lett. 129 (1981) 205–209.
[120] B.-D. Hsu, Y.-S. Lee, J. Photochem. Photobiol. B: Biol. 30 (1995) 57–61.
[121] T. Graan, D.R. Ort, Biochim. Biophys. Acta 852 (1986) 320–330.
[122] J. Cao, Govindjee, Biochim. Biophys. Acta, 1015 (1990) 180–188.
[123] B.-D. Hsu, Y.-S. Lee, Photosynth. Res. 27 (1991) 143–150.
[124] R.A. Chylla, J. Whitmarsh, Plant Physiol. 90 (1989) 765–772.
[125] P. Joliot, Biochim. Biophys. Acta 102 (1965) 116–134.
[126] J. Lavergne, Photobiochem. Photobiophys. 3 (1982) 257–271.
[127] J. Lavergne, Photobiochem. Photobiophys. 3 (1982) 273–285.

[128] B.-D. Hsu, Plant Sci. 81 (1992) 169–174.
[129] B.-D. Hsu, Photosynth. Res. 36 (1993) 81–88.
[130] U. Schreiber, R. Bauer, U.F. Frank, in: G. Forti, M. Avron, A. Melandri (Eds.), Proceedings of the 2nd International Congress on Photosynthesis, Junk, The Hague, 1971, pp. 169–179.
[131] S. Malkin, Biochim. Biophys. Acta 234 (1971) 415–427.
[132] E. Baake, J.P. Schlöder, Bull. Math. Biol. 54 (1992) 999–1021.
[133] V. Goltsev, I. Yordanov, Photosynthetica 33 (1997) 571–586.
[134] B.A. Diner, in: L.A. Staehelin, C.J. Arntzen (Eds.), Photosynthesis III, Encyclopedia of Plant Physiology vol. 19, Springer, Berlin, 1986, pp. 422–436.
[135] D.R. Ort, J. Whitmarsh, Photosynth. Res. 23 (1990) 101–104.
[136] B.A. Diner, V. Petrouleas, J.J. Wendoloski, Physiol. Plant. 81 (1991) 423–436.
[137] L. Nedbal, J. Whitmarsh, Photosynthetica 27 (1992) 57–61.
[138] G. Papageorgiou, Govindjee, Biophys. J., 8 (1968) 1316–1328.
[139] A. Yamagishi, K. Satoh, S. Katoh, Plant Cell Physiol. 19 (1978) 17–25.
[140] D.A. Walker, Planta 153 (1981) 273–278.
[141] D.A. Walker, P. Horton, M.N. Sivak, W.P. Quick, Photobiochem. Photobiophys. 5 (1983) 35–39.
[142] D.A. Walker, M.N. Sivak, R.T. Prinsley, J.K. Cheesbrough, Plant Physiol. 73 (1983) 542–549.
[143] H. Kautsky, U.F. Frank, Biochem. Z. 315 (1943) 176–206.
[144] Y. Zeinalov, L.T. Maslenkova, in: M. Pessarakli (Ed.), Handbook of Photosynthesis, Marcel Dekker, New York, 1996, pp. 129–150.
[145] G. Papageorgiou, Govindjee, Biochim. Biophys. Acta, 234 (1971) 428-432.
[146] J.-M. Briantais, C. Vernotte, M. Picaud, G.H. Krause, Biochim. Biophys. Acta 548 (1979) 128–138.
[147] J.-M. Briantais, C. Vernotte, M. Picaud, G.H. Krause, Biochim. Biophys. Acta 591 (1980) 198–202.
[148] G.H. Krause, C. Vernotte, J.-M. Briantais, Biochim. Biophys. Acta 679 (1982) 116–124.
[149] G.H. Krause, Biochim. Biophys. Acta 333 (1974) 301–313.
[150] G.H. Krause, in: M. Avron (Ed.), Proceedings of the 3rd International Congress on Photosynthesis, Elsevier, Amsterdam, 1975, pp. 1021–1030.
[151] J. Barber, J. Mills, J. Nicholson, FEBS Lett. 49 (1974) 106–110.
[152] J. Barber, A. Telfer, J. Nicholson, Biochim. Biophys. Acta 357 (1974) 161–165.
[153] V.V. Klimov, V.A. Shuvalov, U. Heber, Biochim. Biophys. Acta 809 (1985) 345–350.
[154] P. Horton, A.V. Ruban, R.G. Walters, Annu. Rev. Plant Physiol. Plant Mol. Biol. 47 (1996) 655–684.
[155] P. Pospíšil, Photosynthetica 34 (1997) 343–355.
[156] M. Bradbury, N.R. Baker, Biochim. Biophys. Acta 765 (1984) 271–281.
[157] U. Schreiber, U. Schliwa, W. Bilger, Photosynth. Res. 10 (1986) 51–62.
[158] B. Demmig, K. Winter, Aust. J. Plant Physiol. 15 (1988) 163–177.
[159] W.P. Quick, M. Stitt, Biochim. Biophys. Acta 977 (1989) 287–296.
[160] R.G. Walters, P. Horton, Photosynth. Res. 27 (1991) 121–133.
[161] B. Demmig, O. Björkman, Planta 171 (1987) 171–184.
[162] P. Horton, A. Hague, Biochim. Biophys. Acta 932 (1988) 107–115.
[163] H.K. Lichtenthaler, C. Buschmann, U. Rinderle, G. Schmuck, Radiat. Environ. Biophys. 25 (1986) 297–308.
[164] U. Schreiber, Ch. Neubauer, Z. Naturforsch. 42c (1987) 1255–1264.
[165] R. Delosme, Biochim. Biophys. Acta 143 (1967) 108–128. (in French)
[166] R.J. Strasser, Govindjee, in: J.H. Argyroudi-Akoyunoglou (Ed.), Regulation of Chloroplast Biogenesis Plenum Press, New York, 1991, pp. 423–426.
[167] R.J. Strasser, Govindjee, in: M. Murata (Ed.), Research in Photosynthesis vol. 2, Kluwer, Dordrecht, 1992, pp. 29–32.
[168] A. Stirbet, R.J. Strasser, Arch. Sci. Genève 48 (1995) 41–60.
[169] A. Stirbet, R.J. Strasser, in: First International Symposium on Mathematical Modelling and Simulation in Agriculture and Bio-industries, vol. 1, Brussels, 1995, pp. I.B.2-1–I.B.2-6.
[170] A. Stirbet, Govindjee, B.J. Strasser, R.J. Strasser, in: P. Mathis (Ed.), Photosynthesis: From Light to Biosphere vol. II, Kluwer, Dordrecht, 1995, pp. 912–922.
[171] A. Stirbet, R.J. Strasser, Math. Com. Sim. 42 (1996) 245–253.
[172] D. Lazár, in: M. Lesňák, J. Luňáček, J. Pištora (Eds.), Proceedings of Twelfth Conference of Czech and Slovak Physicists, vol. I, Academic Press, Ostrava, 1996, pp. 96–99 (in Czech).
[173] A. Stirbet, Govindjee, B.J. Strasser, R.J. Strasser, J. Theor. Biol., 193 (1998) 131–151.
[174] B. Ruth, Arch. Hydrobiol. 131 (1994) 297–308.
[175] B. Ruth, Arch. Hydrobiol. 136 (1996) 1–17.
[176] D. Lazár, M. Brokeš, J. Nauš, L. Dvořák, J. Theor. Biol. 191 (1998) 79–86.
[177] B. Ruth, Meas. Sci. Technol. 1 (1990) 517–521.
[178] B. Ruth, Radiat. Environ. Biophys. 30 (1991) 321–332.
[179] X. Barthélemy, R. Popovic, F. Franck, J. Photochem. Photobiol. B: Biol. 39 (1997) 213–218.
[180] H.I. Virgin, Physiol. Plantarum 7 (1954) 560–570.
[181] C. Buschmann, H. Schrey, Photosynth. Res. 1 (1981) 233–241.
[182] R.J. Strasser, B. Schwarz, J.B. Bucher, Eur. J. For. Path. 17 (1987) 149–157.
[183] L.L. France, N.E. Geacintov, J. Breton, L. Valkunas, Biochim. Biophys. Acta 1101 (1992) 105–119.
[184] D. Mauzerall, Biophys. J. 16 (1976) 87–91.
[185] A.C. Ley, D.C. Mauzerall, Biochim. Biophys. Acta 680 (1982) 95–106.

[186] A.C. Ley, D.C. Mauzerall, Biochim. Biophys. Acta 680 (1982) 174–180.
[187] J. Deprez, A. Dobek, N.E. Geacintov, G. Paillotin, J. Breton, Biochim. Biophys. Acta 725 (1983) 444–454.
[188] N.E. Geacintov, G. Paillotin, J. Deprez, A. Dobek, J. Breton, in: C. Sybesta (Ed.), Advances in Photosynthesis Research, M. Nijhoff/Dr. W. Junk, The Hague, 1984, pp. 37–40.
[189] A.C. Ley, D.C. Mauzerall, Biochim. Biophys. Acta 850 (1986) 234–248.
[190] P.G. Falkowski, K. Wyman, A.C. Ley, D.C. Mauzerall, Biochim. Biophys. Acta 849 (1986) 183–192.
[191] D. Mauzerall, N.L. Greenbaum, Biochim. Biophys. Acta 974 (1989) 119–140.
[192] L.L. France, N.E. Geacintov, J. Breton, in: M. Baltscheffsky (Ed.), Current Research in Photosynthesis, vol. I, Kluwer, Dordrecht, 1990, pp. 467–470.
[193] P.W. Hemelrijk, H.J. van Gorkom, in: N. Murata (Ed.), Research in Photosynthesis, vol. II, Kluwer, Dordrecht, 1992, pp. 33–36.
[194] J.-M. Ducruet, Y. Lemoine, Plant Cell Physiol. 26 (1985) 419–429.
[195] N.G. Bukhov, S.C. Sabat, P. Mohanty, Photosynth. Res. 23 (1990) 81–87.
[196] V. Goltsev, I. Yordanov, T. Tsonev, Photosynthetica 30 (1994) 629–643.
[197] B. Guissé, A. Srivastava, R.J. Strasser, in: P. Mathis (Ed.), Photosynthesis: From Light to Biosphere, Vol. IV, Kluwer, Dordrecht, 1995, pp. 913–916.
[198] B. Guissé, A. Srivastava, R.J. Strasser, Arch. Sci. Genève 48 (1995) 147–160.
[199] A. Srivastava, B. Guissé, H. Greppin, R.J. Strasser, Biochim. Biophys. Acta 1320 (1997) 95–106.
[200] B.J. Strasser, Photosynth. Res. 52 (1997) 147–155.
[201] D. Lazár, P. Ilík, J. Nauš, J. Luminesc. 72-74 (1997) 595–596.
[202] D. Lazár, P. Ilík, Plant Sci. 124 (1997) 159–164.
[203] H. Kautsky, R. Eberlein, Biochem. Z. 302 (1939) 137–166.
[204] H. Kautsky, W. Appel, H. Amann, Biochem. Z. 332 (1960) 227–292.
[205] J.H. Golbeck, B. Kok, Biochim. Biophys. Acta 547 (1979) 347–360.
[206] U. Schreiber, Ch. Neubauer, Photosynth. Res. 25 (1990) 279–293.
[207] H. Hormann, Ch. Neubauer, K. Asada, U. Schreiber, Photosynth. Res. 37 (1993) 69–89.
[208] U. Schreiber, H. Hormann, Ch. Neubauer, Ch. Klughammer, Aust. J. Plant Physiol. 22 (1995) 209–220.
[209] P. Haldimann, A. Srivastava, R.J. Strasser, in: P. Mathis (Ed.), Photosynthesis: From Light to Biosphere, vol. II, Kluwer, Dordrecht, 1995, pp. 911–914.
[210] B. Diner, D. Mauzerall, Biochim. Biophys. Acta 305 (1973) 329–352.
[211] D. Nash, M. Takahashi, K. Asada, Plant Cell Physiol. 25 (1984) 531–539.
[212] G.C. Harris, U. Heber, Plant Physiol. 101 (1993) 1169–1173.
[213] V.P. Shinkarev, Ch. Xu, Govindjee, C.A. Wraight, Photosynth. Res., 51 (1997) 43–49.
[214] T. Wydrzynski, Govindjee, Biochim. Biophys. Acta, 387 (1975) 403–408.
[215] P. Jursinic, J. Warden, Govindjee, Biochim. Biophys. Acta, 440 (1976) 322–330.
[216] H. Wincencjusz, S.I. Allakhverdiev, V.V. Klimov, H.J. van Gorkom, Biochim. Biophys. Acta 1273 (1996) 1–3.
[217] V.V. Klimov, R.J. Hulsebosch, S.I. Allakhverdiev, H. Wincencjusz, H.J. van Gorkom, A.J. Hoff, Biochemistry 36 (1997) 16277–16281.
[218] V.V. Klimov, S.V. Baranov, S.I. Allakhverdiev, FEBS Lett. 418 (1997) 243–246.
[219] B.A. Diner, V. Petrouleas, Biochim. Biophys. Acta 1015 (1990) 141–149.
[220] R. Hienerwadel, C. Berthomieu, Biochemistry 34 (1995) 16288–16297.
[221] Govindjee, M.P.J. Pulles, R. Govindjee, H.J. van Gorkom, L.N.M. Duysens, Biochim. Biophys. Acta, 449 (1976) 602–605.
[222] J.J.S. van Rensen, W.J.M. Tonk, S.M. de Bruijn, FEBS Lett. 226 (1988) 347–351.
[223] J.J. Eaton-Rye, Govindjee, Biochim. Biophys. Acta, 935 (1988) 237–247.
[224] J.J. Eaton-Rye, Govindjee, Biochim. Biophys. Acta, 935 (1988) 248–257.
[225] C. Xu, S. Taoka, A.R. Crofts, Govindjee, Biochim. Biophys. Acta, 1098 (1991) 32–40.
[226] M.T. Giardi, T. Kuèera, J.-M. Briantais, M. Hodges, Plant Physiol. 109 (1995) 1059–1068.
[227] X. Deng, A. Melis, Photobiochem. Photobiophys. 13 (1986) 41–52.
[228] D.J. Kyle, P. Haworth, C.J. Arntzen, Biochim. Biophys. Acta 680 (1982) 336–342.
[229] A.R. Crofts, C.A. Wraight, Biochim. Biophys. Acta 726 (1983) 149–185.
[230] Govindjee, M.R. Wasielewski, in: W.R. Briggs (Ed.), Photosynthesis, Alan R. Liss, New York, 1989, pp. 71–103.
[231] B. Kok, B. Forbush, M. McGloin, Photochem. Photobiol. 11 (1970) 457–475.
[232] R.J. Debus, B.A. Barry, I. Sithole, G.T. Babcock, L. McIntosh, Biochemistry 27 (1988) 9071–9074.
[233] J.G. Metz, P.J. Nixon, M. Rögner, G.W. Brudvig, B.A. Diner, Biochemistry 28 (1989) 6960–6969.
[234] B. Bouges-Bocquet, Biochim. Biophys. Acta 314 (1973) 250–256.
[235] B.R. Velthuys, J. Amesz, Biochim. Biophys. Acta 333 (1974) 85–94.
[236] R. van Grondelle, J.P. Dekker, T. Gillbro, V. Sundstrom, Biochim. Biophys. Acta 1187 (1994) 1–65.
[237] G.H. Schatz, H. Brock, A.R. Holzwarth, Biophys. J. 54 (1988) 397–405.
[238] W. Leibl, J. Breton, J. Deprez, H.W. Trissl, Photosynth. Res. 22 (1989) 257–275.

[239] H. Dau, Photochem. Photobiol. 60 (1994) 1–23.
[240] M.R. Wasielewski, D.G. Johnson, M. Seibert, Govindjee, Proc. Natl. Acad. Sci. USA, 86 (1989) 524–528.
[241] T.A. Roelofs, M. Gilbert, V.A. Shuvalov, A.R. Holzwarth, Biochim. Biophys. Acta 1060 (1991) 237–244.
[242] T.A. Roelofs, S.L.S. Kwa, R. van Grondelle, J.P. Dekker, A.R. Holzwarth, Biochim. Biophys. Acta 1143 (1993) 147–157.
[243] H.C. Chang, R. Jankowiak, N.R.S. Reddy, C.F. Yocum, R. Picorel, M. Seibert, G.J. Small, J. Phys. Chem. 98 (1994) 7725–7735.
[244] J.P.M. Schelvis, P.I. van Noort, T.J. Aartsma, H.J. van Gorkom, Biochim. Biophys. Acta 1184 (1994) 242–250.
[245] G.P. Wiederrecht, M. Seibert, Govindjee, M.R. Wasielewski, Proc. Natl. Acad. Sci. USA, 91 (1994) 8999–9003.
[246] W. Haehnel, J.A. Nairn, P. Reisburg, K. Sauer, Biochim. Biophys. Acta 680 (1982) 161–173.
[247] I. Moya, M. Hodges, J.-C. Barbet, FEBS Lett. 198 (1986) 256–262.
[248] M. Hodges, I. Moya, Biochim. Biophys. Acta 849 (1986) 193–202.
[249] R. Bassi, M. Silvestri, P. Dainese, G.M. Giacometti, I. Moya, J. Photochem. Photobiol. B: Biol. 9 (1991) 335–354.
[250] K. Brettel, E. Schlodder, H.T. Witt, Biochim. Biophys. Acta 766 (1984) 403–415.
[251] B. Mayer, E. Schlodder, J.P. Dekker, H.T. Witt, Biochim. Biophys. Acta 974 (1989) 36–43.
[252] G.T. Babcock, R.E. Blankenship, K. Sauer, FEBS Lett. 61 (1976) 286–289.
[253] B.R. Velthuys, in: G. Akoyunoglou (Ed.), Photosynthesis, vol. II, Balaban International Science Service, Philadelphia, 1981, pp. 75–85.
[254] J. Lavergne, FEBS Lett. 173 (1984) 9–14.
[255] J.P. Dekker, J.J. Plijter, L. Ouwehand, H.J. van Gorkom, Biochim. Biophys. Acta 767 (1984) 176–179.
[256] G. Renger, W. Weiss, Biochim. Biophys. Acta 850 (1986) 184–196.
[257] J. Cole, K. Sauer, Biochim. Biophys. Acta 891 (1987) 40–48.
[258] Ö. Saygin, H.T. Witt, Biochim. Biophys. Acta 893 (1987) 452–469.
[259] C.W. Hoganson, G.T. Babcock, Biochemistry 27 (1988) 5848–5855.
[260] G. Renger, B. Hanssum, FEBS Lett. 299 (1992) 28–32.
[261] F. Rappaport, M. Blanchard-Desce, J. Lavergne, Biochim. Biophys. Acta 1184 (1994) 178–192.
[262] M.R. Razeghifard, Ch. Klughammer, R.J. Pace, Biochemistry 36 (1997) 86–92.
[263] H.-W. Trissl, Photosynth. Res. 47 (1996) 175–185.
[264] Ch.J. Law, R.J. Cogdell, H.-W. Trissl, Photosynth. Res. 52 (1997) 157–165.
[265] D. Mauzerall, Proc. Natl. Acad. Sci. USA 69 (1972) 1358–1362.
[266] K. Zankel, Biochim. Biophys. Acta 325 (1973) 138–148.
[267] J. Bowes, A.R. Crofts, Biochim. Biophys. Acta 590 (1980) 373–384.
[268] J. Bowes, A.R. Crofts, C.J. Artnzen, Arch. Biochem. Biophys. 200 (1980) 303–308.
[269] H.H. Robinson, A.R. Crofts, FEBS Lett. 153 (1983) 221–226.
[270] W. Weiss, G. Renger, in: C. Sybesta (Ed.), Advances in Photosynthesis Research, M. Nijhoff/Dr. W. Junk, The Hague, 1984, pp. 167–170.
[271] S. Taoka, A.R. Crofts, in: M. Baltscheffsky (Ed.), Current Research in Photosynthesis, vol. I, Kluwer, Dordrecht, 1990, pp. 547–550.
[272] A.R. Crofts, I. Bartoli, D. Kramer, S. Taoka, Z. Naturforsch. 48c (1993) 259–266.
[273] M. Haumann, W. Junge, FEBS Lett. 347 (1994) 45–50.
[274] B.A. Diner, in: M. Avron (Ed.), Proceedings of the 3rd International Congress on Photosynthesis, Elsevier, Amsterdam, 1975, pp. 589–601.
[275] B. Bouges-Bocquet, in: M. Avron (Ed.), Proceedings of the 3rd International Congress on Photosynthesis, Elsevier, Amsterdam, 1975, pp. 579–588.
[276] J.A. van Best, L.N.M. Duysens, Biochim. Biophys. Acta 408 (1975) 154–163.
[277] B.A. Diner, Biochim. Biophys. Acta 460 (1977) 247–258.
[278] H.H. Stiehl, H.T. Witt, Z. Naturforsch. 24 (1969) 1588–1598.
[279] P. Joliot, A. Joliot, in: Y. Inoue, A.R. Crofts, Govindjee, N. Murata, G. Renger, K. Satoh (Eds.), The Oxygen Evolving System of Photosynthesis, Academic Press, Tokyo, 1983, pp. 359–368.
[280] W. Haehnel, Annu. Rev. Plant Physiol. 35 (1984) 659–693.
[281] R. Mitchell, A. Spillmann, W. Haehnel, Biophys. J. 58 (1990) 1011–1024.
[282] P. Joliot, J. Lavergne, D. Béal, Biochim. Biophys. Acta 1101 (1992) 1–12.
[283] J. Lavergne, J.-P. Bouchaud, P. Joliot, Biochim. Biophys. Acta 1101 (1992) 13–22.
[284] B. Kok, P. Joliot, M. McGloin, in: H. Metzner (Ed.), Proceedings of the 1st International Congress on Photosynthesis, Laup, Tubingen, 1969, pp. 1042–1056.
[285] W. Haehnel, Biochim. Biophys. Acta 440 (1976) 506–521.
[286] B. Bouges-Bocquet, Biochim. Biophys. Acta 462 (1977) 371–379.
[287] B.R. Velthuys, Proc. Natl. Acad. Sci. USA 76 (1979) 2765–2769.
[288] J. Whitmarsh, J.R. Bowyer, A.R. Crofts, Biochim. Biophys. Acta 682 (1982) 404–412.
[289] H.J. van Gorkom, Photosynth. Res. 6 (1985) 97–112.
[290] G.N. Johnson, A.W. Rutherford, A. Krieger, Biochim. Biophys. Acta 1229 (1995) 202–207.
[291] R. Emerson, W. Arnold, J. Gen. Physiol. 16 (1932) 191–205.
[292] H. Gaffron, K. Wohl, Naturwissenschften 24 (1936) 81–90.
[293] J. Myers, Photosynth. Res. 40 (1994) 303–310.
[294] S. Malkin, Biophys. Chem. 2 (1974) 327–337.

[295] W.J. Vredenberg, L.N.M. Duysens, Nature 197 (1963) 355–357.
[296] L.N.M. Duysens, in: G. Wolstenholme, D.W. Fitzzimons (Eds.), Chlorophyll Organisation and Energy Transfer in Photosynthesis, Ciba Foundation Symposium 61, Excerpta Medica, Amsterdam, 1979, pp. 323–340.
[297] D. Mauzerall, J. Phys. Chem. 80 (1976) 2306–2309.
[298] C.E. Swenberg, N.E. Geacintov, M. Pope, Biophys. J. 16 (1976) 1447–1452.
[299] G. Paillotin, C.E. Swenberg, J. Breton, N.E. Geacintov, Biophys. J. 25 (1979) 513–534.
[300] A. Joliot, P. Joliot, C.R. Acad. Sci. Paris 258D (1964) 4622–4625. (in French)
[301] P. Joliot, P. Bennoun, A. Joliot, Biochim. Biophys. Acta 305 (1973) 317–328.
[302] R.T. Wang, J. Myers, Photochem. Photobiol. 17 (1973) 321–332.
[303] I. Moya, Biochim. Biophys. Acta 368 (1974) 214–227.
[304] G. Paillotin, J. Theor. Biol. 58 (1976) 237–252.
[305] M. Hipkins, Biochim. Biophys. Acta 502 (1978) 514–523.
[306] W.L. Butler, M. Kitajama, Biochim. Biophys. Acta 396 (1975) 72–85.
[307] V.V. Klimov, A.V. Klevanik, V.A. Shuvalov, A.A. Krasnovsky, FEBS Lett. 82 (1977) 183–186.
[308] V.V. Klimov, S.I. Allakhverdiev, V.Z. Paschenko, Dokl. Akad. Nauk SSSR 242 (1978) 1204–1207. (in Russian)
[309] V.V. Klimov, A.A. Krasnovskij, Photosynthetica 15 (1981) 592–609.
[310] J. Breton, FEBS Lett. 159 (1983) 1–5.
[311] J. Breton, FEBS Lett. 147 (1982) 16–20.
[312] G. Renger, in: J. Barber (Ed.), The Photosystems: Structure, Function and Molecular Biology, Elsevier, Amsterdam, 1992, pp. 45–99.
[313] U. Schreiber, A. Krieger, FEBS Lett. 397 (1996) 131–135.
[314] G. Paillotin, in: D.O. Hall, J. Coombs, T.W. Goodwin (Eds.), Photosynthesis '77, The Biochemical Society, London, 1978, pp. 33–44.
[315] R.J. Strasser, in: G. Akyonoglou (Ed.), Chloroplast Development, Elsevier, Amsterdam, 1978, pp. 513–524.
[316] R.J. Strasser, in: G. Akyonoglou (Ed.), Proceedings of the 5th International Congress on the Photosynthesis, vol. 3, Balaban International Science Service, Philadelphia, 1981, pp. 727–737.
[317] R.J. Strasser, P. Eggenberg, K. Pfister, Govindjee, Arch. Sci. Genève, 45 (1992) 207–224.
[318] B.-D. Hsu, Biochim. Biophys. Acta 1140 (1992) 30–36.
[319] G. Renger, A. Schulze, Photobiochem. Photobiophys. 9 (1985) 79–87.
[320] R.J. Strasser, A. Stirbet, in: I. Farkas (Ed.), Proceedings of the Second International Symposium on Mathematical Modelling and Simulation in Agriculture and Bio-Industries, Budapest, 1997, pp. 21–26.
[321] P.G. Falkowski, Z. Kolber, D.C. Mauzerall, Biophys. J. 66 (1994) 923–925.
[322] H.-W. Trissl, Biophys. J. 66 (1994) 925–926.
[323] Erratum, Biophys. J., 65 (1993) 982–983.
[324] E. Baake, R.J. Strasser, in: M. Baltscheffsky (Ed.), Current Research in Photosynthesis, vol. II, Kluwer, Dordrecht, 1990, pp. 567–570.
[325] E. Pfündel, Photosynth. Res. 56 (1998) 185–195.
[326] R.P. Hemenger, R.M. Pearlstein, K. Lakatos-Lindenberg, J. Math. Phys. 13 (1972) 1056–1063.
[327] G. Paillotin, J. Theor. Biol. 36 (1972) 223–235.
[328] R.S. Knox, in: J. Barber (Ed.), Primary Processes of Photosynthesis Elsevier, Amsterdam, 1977, pp. 55–97.
[329] R.C. Jennings, M. Flavio, L. Finzi, G. Zucchelli, Photosynth. Res. 47 (1996) 167–173.
[330] Govindjee, J. Amesz, R.S. Knox (Eds.), Photosynth. Res., 48 (1996) 1–319.
[331] G.W. Robinson, Brookhaven Symp. Biol. 19 (1967) 16–48.
[332] D.M. Vavilin, E. Tyystjärvi, A.-M. Aro, Biophys. J. 75 (1998) 503–512.
[333] D. Lazár, P. Pospíšil, Eur. Biophys. J. (1999), in press.
[334] D. Lazár, Doctoral Thesis, Palacký University, Olomouc, Czech Republic, 1999.